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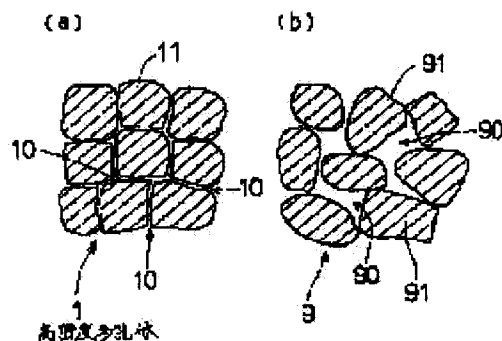
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(54) HIGH DENSITY POROUS BODY AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To produce a porous body having high bulk density, uniform in pore diameter and capable of satisfactorily exhibiting its characteristics at the time of use as an adsorbent or a catalyst.

SOLUTION: Alkoxysilane, water and a surfactant as starting materials are mixed so that the molar ratio of H₂O to Si is regulated to ≤ 10 and they are brought into a reaction to form a silica-surfactant composite. The surfactant is then removed from the composite to produce the objective high density porous body 1 having ≥ 0.5 g/cc bulk density. Pore diameter at the highest peak of the pore diameter distribution curve of the porous body 1 is within the range of 1-10nm and pores accounting for $\geq 60\%$ of the total pore volume existing within the pore diameter range of (the pore diameter at the highest peak) $\pm 40\%$.



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CLAIMS

[Claim(s)]

[Claim 1] The high density porous body which 60% or more of total pore volume is contained in pole diameter within the limits of -40 - +40% of the pole diameter which is in within the limits whose pole diameter which shows the greatest peak in a pore-volume-distribution curve is 1-10nm, and shows the greatest peak in the above-mentioned pore-volume-distribution curve, and is further characterized by bulk density being 0.5g/cc or more.

[Claim 2] The high density porous body characterized by amount-of-adsorption change when it is in within the limits whose pole diameter which shows the greatest peak in a pore-volume-distribution curve is 1-10nm and relative vapor pressure changes 0.2 times in steam adsorption isotherm having a part 0.1g [/cc] or more.

[Claim 3] The high density porous body characterized by having one or more peaks in whenever [angle-of-diffraction / which is in within the limits whose pole diameter which shows the greatest peak in a pore-volume-distribution curve is 1-10nm, and is equivalent to d value of 1nm or more within the limits in a powder X diffraction pattern].

[Claim 4] The above-mentioned high density porous body is a high density porous body characterized by more than 80wt% of the whole consisting of silicon and oxygen in any 1 term of claims 1-3.

[Claim 5] The manufacture approach of the high density porous body which mix, and the alkoxysilane, the water, and the surfactant which are a raw material are made to react, forms a silica / surfactant complex, and is subsequently characterized by the H2 O/Si mole ratio in the above-mentioned raw material being ten or less in the approach of manufacturing a high density porous body by removing a surfactant from the above-mentioned silica / surfactant complex.

[Claim 6] It is the manufacture approach of the high density porous body characterized by the above-mentioned alkoxysilane being a tetramethoxy silane in claim 5.

[Claim 7] It is the manufacture approach of the high density porous body characterized by being the compound with which the above-mentioned surfactant has a long-chain alkyl group and a hydrophilic group in claim 5 or 6.

[Claim 8] It is the manufacture approach of the high density porous body characterized by the above-mentioned surface active agent being alkyl trimethylammonium in claim 7.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a high density porous body usable as a catalyst which can be used for the adsorbent which can be used for recovery of a solvent, a gasoline, etc., adsorption heat pump, temperature control, water treatment, deodorization, etc., reforming, cracking of purification of exhaust gas, organic synthesis, and petroleum, etc., and its manufacture approach.

[0002]

[Description of the Prior Art] The porous body which is in the range especially whose pole diameter (the diameter of pore is meant in this specification.) is 1-10nm in a porous body, and is distributed over the range where the above-mentioned pole diameter is especially narrow is called a meso porous body. There is the approach of making a surfactant act on stratified silicate and manufacturing as the manufacture approach of the above-mentioned meso porous body, for example (JP,4-238810,A, JP,6-24867,A). Moreover, there is also a method of making a silica and Si alkoxide react with a surfactant, and manufacturing them (JP,5-503499,A).

[0003]

[Problem(s) to be Solved] However, by the conventional manufacture approach, only the small meso porous body of bulk density was able to be manufactured. Therefore, when these meso porous bodies were used as an adsorbent or a catalyst, the restoration container for holding an adsorbent or a catalyst etc. was able to be filled up only with the comparatively little meso porous body. In this case, the engine performance of the above-mentioned meso porous body was not able to be made to discover enough.

[0004] Moreover, in order to make the engine performance of the above-mentioned meso porous body discover enough, enlarging the restoration container filled up with this meso porous body is also considered. However, the problem that the equipment (for example, adsorption heat pump) which contains this restoration container etc. will be enlarged because a restoration container etc. becomes large had arisen.

[0005] In case bulk density is high, has a uniform pole diameter and uses this invention as an adsorbent or a catalyst in view of this trouble, it tends to offer the high density porous body which can discover the property enough, and its manufacture approach.

[0006]

[Means for Solving the Problem] 60% or more of total pore volume is contained in pole diameter within the limits of -40 - +40% of the pole diameter which is in within the limits whose pole diameter which shows the greatest peak in a pore-volume-distribution curve is 1-10nm, and shows the greatest peak in the above-mentioned pore-volume-distribution curve, and the high density porous body further characterized by bulk density being 0.5g/cc or more has invention of claim 1.

[0007] It explains below about an operation of this invention. The high density porous body of this invention has the above-mentioned description in the pore-volume-distribution curve mentioned later. Moreover, the bulk density is within the limits of specification. As the high density porous body which fulfills such conditions is shown in below-mentioned drawing 1 (a), it is constituted when the primary particles of the submicron order which has pore so much gather, and the clearance between these primary particles is very small, or hardly exists.

[0008] On the other hand, the meso porous body with the conventional low bulk density mentioned above has the structure which had a big clearance among the primary particles of the same submicron order as the above, as shown in drawing 1 (b). An adsorption property or a catalyst property peculiar to the above-mentioned meso porous body etc. is mainly discovered by the pore inside a primary particle. The high density porous body of this invention has a very small clearance between the primary particles which are unrelated to the manifestation of an adsorption property or a catalyst property, or has the structure which hardly exists. For this reason, high structure of bulk density can be realized in the high density porous body of this invention, without spoiling an adsorption property or a catalyst property.

[0009] As mentioned above, in case according to this invention bulk density is high, has a uniform pole diameter and uses it as an adsorbent or a catalyst, the high density porous body which can discover the property enough can be obtained.

[0010] Moreover, the above is further explained to a detail. First, generally in the adsorption isotherm of the steam in a meso porous body, it is known that adsorption/desorption of a steam will occur [relative vapor pressure (P/P0)] rapidly in 0.1-0.81. And it can be drawn from the relation of the pole diameter and relative vapor pressure in the Kelvin equation whether the adsorption isotherm of a certain specific meso porous body fulfills the above-mentioned conditions.

[0011] The Kelvin equation is a formula showing the relation between the pore radius (r) of a meso porous body, and the relative vapor pressure (P/P0) from which an adsorbate starts capillary condensation, and the following (1) types can show here.

$$\ln(P/P_0) = (2V_L \gamma \cos \theta) / (rRT) \dots (1)$$

In addition, for molar volume when Above VL has a liquid adsorbate, and gamma, surface tension when an adsorbate is liquid, and theta are [a gas constant and T of a contact angle and R] absolute temperature.

[0012] When an adsorbate is a steam, the numeric value of VL=18.05 and 10-6m3 / mol, gamma=72.59 and 10-3 N/m, R=8.3143 J/deg-mol, and theta= 0 can be substituted here at (1) type. Consequently, the above-mentioned (1) formula

is $\ln(P/P_0) = -1.058/r$ used as the following (2) types... (2)

In addition, the unit of r is nm.

[0013] The above-mentioned (2) formula shows generating in the range of P/P_0 with narrower adsorption/desorption of a steam, when distributed over the range where a pole diameter is more narrow in pore volume distribution. That is, the difference of P/P_0 in adsorption isotherm adsorption starts P/P , and P/P_0 to which adsorption reached saturation is small.

[0014] It is in within the limits the pole diameter of whose is 1-10nm in the high density porous body of this invention. And when a pole diameter is in the range which is 1-10nm from the above-mentioned (2) formula, it turns out that the range of P/P_0 which starts adsorption/desorption of the steam in adsorption isotherm is set to 0.12-0.81. This range is range which adsorption/desorption of a steam produce rapidly, as mentioned above. Thereby, it turns out that it has the property that the amount of adsorption changes a lot by the change of small P/P_0 with the high density porous body (P/P_0 setting in the range of 0.12-0.81) of this invention optimal as an adsorbent in adsorption heat pump, a thermoregulator, etc.

[0015] In addition, it explains below per above-mentioned pore distribution curve. The above-mentioned pore-volume-distribution curve shows the curve which plotted the value (dV/dD) which differentiated the pore volume (V) of a meso porous body with the pole diameter (D) to the pole diameter (D) (refer to drawing 3). The above-mentioned pore-volume-distribution curve can be created by the gas adsorption method shown below. In addition, the gas best used in the describing [above] gas adsorption method is nitrogen.

[0016] First, at liquid nitrogen temperature (-196 degrees C), nitrogen gas is introduced and the target meso porous body is asked for the amount of adsorption in the amount method of constant volume, or a weight method. Then, the pressure of the nitrogen gas to introduce is made to increase gradually, and adsorption isotherm is created by plotting the amount of adsorption of nitrogen gas to each equilibrium pressure. Cranston-Inclay from this adsorption isotherm — law and Pollimore-Heal — drawing the above-mentioned pore-volume-distribution curve using the calculus of law — things are made.

[0017] Next, the expression in above-mentioned claim 1 "60% or more of total pore volume is contained in the diameter range of $\pm 40\%$ of the diameter which shows the greatest peak in the above-mentioned pore-volume-distribution curve" is expressing the following conditions. For example, the meso porous body alpha from which the greatest peak in the pore-volume-distribution curve mentioned above is set to 2.7nm is assumed. It asks for the pore volume V which summed up the volume of the pore which has a pole diameter in the range of $1.62 (= 2.7 \times 0.6) - 3.78 (= 2.7 \times 1.4)$ nm in this meso porous body alpha. On the other hand, in the above-mentioned meso porous body alpha, the grand total V_{all} of total pore volume is searched for.

[0018] And when the value of V/V_{all} is more than 0.6 (60%) temporarily, it can be said that it is one of the high density porous bodies which require the above-mentioned meso porous body alpha for this invention. Or in the pore-volume-distribution curve of the above-mentioned meso porous body alpha, also when the integral value of the range where a pole diameter becomes 1.62-3.78nm is 60% or more of a total integral area of a pore-volume-distribution curve, it can be said that the above-mentioned meso porous body alpha is a high density porous body concerning this invention.

[0019] Since the high density porous body of this invention which fulfills such conditions is distributed over the range where a pole diameter is narrow, it can acquire the effectiveness that the amount of adsorption changes a lot, to change of small P/P_0 . In addition, when contained less than 60% of total pore volume, the amount-of-adsorption change to change of P/P_0 is small in the diameter range of $\pm 40\%$ of the diameter which shows the greatest peak in the above-mentioned pore-volume-distribution curve, and a possibility that neither a gas conditioning function nor an adsorption heat pump property may be discovered enough is in it.

[0020] Moreover, the bulk density of the high density porous body of this invention is 0.5g/cc or more. For this reason, in case the above-mentioned high density porous body is used as an adsorbent or a catalyst, a restoration container can be filled up with a lot of high density porous bodies as compared with the former. The manifestation of a thereby more high adsorption property or a catalyst property is attained. Or it becomes possible to make small the restoration container of a high density porous body etc., and the equipment which sets this restoration container etc. can be made small.

[0021] In addition, when the above-mentioned bulk density is less than 0.5g/cc, in order to be able to fill up a restoration container etc. only with a little high density porous body, and not to fully discover a required property or to secure a required property, there is a possibility that it is necessary to enlarge a restoration container, and equipment may be enlarged, for example, mount may become difficult.

[0022] As mentioned above, it turns out that the high density porous body of this invention has the outstanding effectiveness like the above so that it may be known.

[0023] Next, it is desirable that amount-of-adsorption change when it is in within the limits whose pole diameter which shows the greatest peak in a pore-volume-distribution curve is 1-10nm like invention of claim 2 and relative vapor pressure changes 0.2 times in steam adsorption isotherm has a part 0.1g [/cc] or more. The effectiveness that humidity control and an adsorption heat pump property are discovered by the thereby more little porous body can be acquired. In addition, when the above-mentioned amount-of-adsorption change is less than 0.1g/cc, a lot of porous bodies are needed, and there is a possibility of producing the problem that a restoration container and the whole equipment are enlarged.

[0024] With in addition, the above "amount-of-adsorption change when relative vapor pressure changes 0.2 times has a part 0.1g [/cc] or more" When it presupposes that the amounts of adsorption in case relative vapor pressure (P/P_0) is 0.1 and 0.3 are $V_{0.1} = 0.2\text{g/cc}$ and $V_{0.3} = 0.5\text{g/cc}$, respectively in steam adsorption isotherm, It is the semantics of amount-of-adsorption change when relative vapor pressure changes 0.2 times being set to $V_{0.3} - V_{0.1} = 0.3\text{g/cc}$, and corresponding in "0.1g/cc or more." Change of relative vapor pressure may be good even in the range of 0 - 1 throat, and amount-of-adsorption change may be [a part 0.1g //cc / or more] a part of high density porous body.

[0025] Next, it is desirable to have one or more peaks in whenever [angle-of-diffraction / which is in within the limits whose pole diameter which shows the greatest peak in a pore-volume-distribution curve is 1-10nm like invention of claim 3, and is equivalent to d value of 1nm or more within the limits in a powder X diffraction pattern]. This shows that the periodic crystal structure 1nm or more exists in a high density porous body, and is in the range whose pole diameter is 1-10nm, and shows that it is distribution with a uniform pole diameter. It turns out that it has the property which was excellent within the limits of P/P_0 with a narrow steam etc. by this as the adsorption heat pump of causing

** and desorption, or a gas conditioning agent.

[0026] Next, as for the above-mentioned high density porous body, it is desirable like invention of claim 4 that more than 80wt% of the whole consists of silicon and oxygen. Thereby, association with an admolecule (for example, water molecule) and a porous body front face will become comparatively weak, and the molecule to which it stuck tends comparatively] to ****, and it can repeat ** and desorption reversibly. In addition, when the content of silicon and oxygen is less than [80wt%], by mixing a different element from silicon and oxygen, solid acid nature etc. is discovered by the front face and there is a possibility that an admolecule may not **** easily.

[0027] Next, invention of claim 5 is mixed, makes the alkoxysilane, the water, and the surfactant which are a raw material react, forms a silica / surfactant complex, and is in the manufacture approach of the high density porous body characterized by the H₂ O/Si mole ratio in the above-mentioned raw material being ten or less in the approach of subsequently manufacturing a high density porous body by removing a surfactant from the above-mentioned silica / surfactant complex.

[0028] The above "the H₂ O/Si mole ratio in a raw material" shows the ratio of the total amount of Si contained in other raw materials to the total amount of added H₂ O in mixing of the above-mentioned raw material. When the above "an H₂ O/Si mole ratio" is ten or less shows that the consistency of the manufactured porous body can be raised. In addition, the above "an H₂ O/Si mole ratio" becomes [alkoxysilane / the clearance between the particles of the generated silica which carries out hydrolysis and condensation] large in being larger than 10, and there is a possibility that the consistency of the generated silica may fall, as a result. Therefore, there is a possibility that it may become impossible to obtain a high density porous body.

[0029] Moreover, as for the minimum of the above "an H₂ O/Si mole ratio", it is desirable that it is one or more. When the above-mentioned value is less than one, hydrolysis of alkoxysilane does not take place but there is a possibility that a silica may not be obtained as a result. Therefore, there is a possibility that it may become impossible to obtain a high density porous body.

[0030] Next, it is desirable to add a surfactant, after adding water to alkoxysilane first and stirring at a room temperature especially as the mixed approach of the above-mentioned raw material for 10 minutes to 3 hours, although not limited. Moreover, as for the above-mentioned water, it is desirable that 0.5-10 mols add to one mol of silicon which the above-mentioned alkoxysilane contains. When alkoxysilane condenses slowly through a straight chain-like alkoxysilane polymerization object by this mixed approach, the organization of a precise silica is formed and the effectiveness that a consistency increases can be acquired.

[0031] When the addition of the above-mentioned water is less than 0.5 mols, hydrolyzing [of alkoxysilane] becomes inadequate, the frame of a firm high density porous body is not formed, or there is a possibility that the consistency of a porous body may fall. On the other hand, when it adds more mostly than ten mols, hydrolysis and condensation of alkoxysilane are performed quickly and there is a possibility that the consistency of a rough next door high density porous body may fall [a silica organization].

[0032] Moreover, when the above-mentioned mixing time is less than 10 minutes, there is a possibility that the consistency of a high density porous body may fall. On the other hand, when 3 hours is exceeded, there is a possibility that uniform pore may not be formed.

[0033] Furthermore, it is desirable to add a small amount of acid as a pH regulator in the case of the above-mentioned mixing. Thereby, it becomes easy to dissolve each component and becomes easy to prepare a uniform solution. And as for pH in the case of the above-mentioned mixing, it is desirable to be adjusted to the range of 1-4. When Above pH is less than one, hydrolysis and condensation advance quickly and there is a possibility that formation of uniform pore may be barred. Or there is a possibility that the consistency of the generated porous body may fall. On the other hand, when Above pH is larger than 4, the dissolution of each component is inadequate and there is a possibility that required hydrolysis may not be performed. Moreover, as the above-mentioned acid, although dilute hydrochloric acid (for example, two conventions) can be used, other acids, such as a sulfuric acid, are sufficient.

[0034] Moreover, it may be made to dissolve in little water and the above-mentioned surfactant may be added, although you may add with powder. And as for the addition of the above-mentioned surfactant, it is desirable to add to one mol of Si contained in [all] a raw material, so that it may become 1-10 mols. When there are more additions of the above-mentioned surfactant than ten mols, the excessive surfactant which is not contributed to formation of the above-mentioned silica / surfactant complex is intermingled in the above-mentioned silica / surfactant complex, and or the consistency of a high density porous body falls, there is a possibility that a manufacturing cost may become high.

[0035] On the other hand, when the above-mentioned addition is less than one mol, the silica of the surplus which does not contribute to formation of the above-mentioned silica / surfactant complex is intermingled in the above-mentioned silica / surfactant complex, the ratio of the part in which uniform pore is formed falls, and there is a possibility that a required function may not be discovered enough. Furthermore, the above-mentioned silica forms a thick layer in the front face of a silica/surfactant, and adheres to it, and there is also a possibility that the pore volume of the high density porous body obtained by this may decrease.

[0036] Subsequently, a surfactant is removed from the above-mentioned silica / surfactant complex, and it is explained as a high density porous body per [to make] approach. That is, although the above-mentioned silica / surfactant complex are generated in the solution which mixed the raw material, first of all, a silica / surfactant complex is separated out of this solution. Then, a surfactant is removed from obtained independent silica / surfactant complex, and it makes with a high density porous body. It explains below about these processes.

[0037] First, the solution containing a silica/surfactant is solidified while the whole solution had maintained the uniform condition gradually, when it was left as it is. Therefore, the above-mentioned solution becomes massive by leaving the above-mentioned solution in a well-closed container or an open container. It grinds, after drying the lump obtained by this. Furthermore, after that, it applies to a screen and the particle size of a grinding object is arranged. Thereby, the silica / surfactant complex of the shape of powder which has a desired particle size can be obtained.

[0038] Moreover, on the substrate which consists of aluminum etc., the coat of the above-mentioned solution is carried out, and it is left. Thereby, it can solidify on a substrate and the above-mentioned solution can obtain film-like a silica / surfactant complex. In addition, as an approach of carrying out the coat of the solution to the above-mentioned substrate, a spin coat method, the casting method, a dip coating method, etc. can mention.

[0039] next, the above -- a surfactant is removed from the silica / surfactant complex of the shape of powdered or film, and it makes with a high density porous body. As this removal approach, the approach by baking and the approach of using a solvent mention, and it is *****, for example. First, the removal approach by baking is shown. The

above-mentioned silica / surfactant complex are preferably heated in 500 degrees C – 700 degrees C in 400 degrees C – 1000 degrees C. The above-mentioned heating time can remove a surfactant to extent which does not interfere on 30 minutes or more, then practical use. However, in order to remove the above-mentioned surfactant completely, heating for 1 hour or more is more desirable than the above-mentioned silica / surfactant complex.

[0040] Moreover, since temperature is too low when whenever [above-mentioned stoving temperature] is less than 400 degrees C, there is a possibility that combustion removal of the surfactant cannot fully be carried out. Moreover, since temperature is too high when whenever [above-mentioned stoving temperature] exceeds 1000 degrees C, there is a possibility that pore structure may collapse. In addition, the ambient atmosphere which is in charge of the above-mentioned heating should just circulate air. However, since a lot of combustion gas occurs, it is more desirable to circulate inert gas, such as nitrogen gas, the early stages of heating.

[0041] Next, the removal approach which uses a solvent is shown. First, the solvent which added the little cation component to the solvent with large solubility to a surfactant is created. The above-mentioned solvent is made to distribute the above-mentioned silica / surfactant complex, and it stirs. Thereby, a surfactant dissolves and dissociates from the above-mentioned silica / surfactant complex into a solvent. Then, solid content is collected from the above-mentioned solvent. It is the high density porous body for which the above-mentioned solid content asks.

[0042] As the above-mentioned solvent, alcohol, such as ethanol and a methanol, an acetone, etc. can be used, for example. Moreover, in order to add the above-mentioned cation component to a solvent, it is desirable to add the following matter to this solvent. As the above-mentioned matter, a hydrochloric acid, an acetic acid, a sodium chloride, potassium chloride, etc. can be used. The above-mentioned surfactant can be separated from the above-mentioned silica / surfactant complex thereby much more efficiently.

[0043] And as for the addition concentration of the above-mentioned cation, it is desirable to carry out in 0.1–10 mols/l. to the above-mentioned solvent. When the above-mentioned addition concentration is less than 0.1 mols/l., separation of a surfactant is inadequate and there is a possibility that a surfactant may remain in a high density porous body. On the other hand, when the above-mentioned addition concentration is larger than 1. ten mols /, there is a possibility of there being no effectiveness added more than it, and becoming cost quantity. Moreover, there is a possibility that the silica frame of a high density porous body may collapse.

[0044] Next, as for the variance of a silica / surfactant complex to the above-mentioned solvent, it is desirable that they are 0.5–50g to 100 cc of solvents. In being less than 0.5g, the processing effectiveness of a silica / surfactant complex is bad, and there is a possibility that the cost and the manufacturing cost of a solvent may be applied. On the other hand, in [than 50g] more, separation of a surfactant is inadequate and there is a possibility that a surfactant may remain in a high density porous body.

[0045] Moreover, it is desirable to perform stirring after making the above-mentioned solvent distribute a silica / surfactant complex in a 25–100-degree C temperature requirement. Thereby, the processing time can be shortened for separation of a surfactant. When the above-mentioned temperature is less than 25 degrees C, there is a possibility that compaction of the processing time may not be expected. On the other hand, when 100 degrees C is exceeded, the energy cost for heating starts or there is a possibility that the loss by volatilization of a solvent may increase.

[0046] In addition, the above-mentioned high density porous body can be used as powder, and can be screened and fabricated in the configuration according to the purpose of use for every particle size of the. And the process of these sieving and shaping can be performed before the process which removes the above-mentioned surfactant. In this case, collapse of the pore at the time of shaping is barred, or the effectiveness that shaping reinforcement improves can be acquired. Moreover, after fabricating the above-mentioned silica/surfactant in the configuration finally demanded, a surfactant can be removed and it can also consider as a high density porous body. In this case, collapse of the pore at the time of shaping can be prevented. Moreover, shaping reinforcement can be raised.

[0047] Next, as alkoxysilane in the above-mentioned raw material, alkyl alkoxysilane, such as a tetramethoxy silane, a tetra-ethoxy silane, tetra-propoxysilane, or methyl trimetoxysilane, etc. can be used. One kind or two kinds or more of such combination is sufficient.

[0048] And as for especially the above-mentioned alkoxysilane, according to invention of claim 6, it is desirable that it is a tetramethoxy silane. A high density porous body can be manufactured thereby comparatively easily.

[0049] Moreover, as for the above-mentioned surfactant, it is desirable like invention of claim 7 that it is the compound which has a long-chain alkyl group and a hydrophilic group. By using this compound, the effectiveness that the molecular assembly of a surfactant is formed in a reaction solution, and the 1–10nm uniform pore corresponding to the magnitude of that molecular assembly is formed in a high density porous body can be acquired.

[0050] Moreover, as the above-mentioned alkyl group, the thing of 2–18 has a desirable carbon atomic number. By using the surfactant which consists of these alkyl groups, the effectiveness that the above-mentioned molecular assembly is formed efficiently can be acquired. In addition, when there are more above-mentioned carbon atomic numbers than 18, such a surfactant is not marketed but has a possibility that cost may start. Moreover, when a carbon atomic number is 1 (i.e., when the above-mentioned alkyl group is a methyl group), there is a possibility that the above-mentioned molecular assembly may be hard to be formed, and 1–10nm uniform pore may not be formed. Moreover, as the above-mentioned hydrophilic group, $-N+3(CH_3)$, $=N+2(CH_3)$, $**N+**(CH_3)N+$, $-NH_2$, $-NO$, $-OH$, $-COOH$, etc. are mentioned, for example.

[0051] Next, as the above-mentioned surfactant, the compound shown in the following chemical formulas can be used. Moreover, it is desirable like invention of claim 8 as such a compound to use alkyl trimethylammonium.

$C_n H_{2n+1}-N(CH_3)_3 X$ — n is the integer of 2–18 and X is halogenide ion, such as chloride ion and bromide ion, here.

[0052] By using such a surfactant, the effectiveness that the molecular assembly of a surfactant is efficiently formed in a reaction solution, and the 1–10nm uniform pore corresponding to the molecular assembly is easy to be formed can be acquired. In addition, as an example of a surface active agent with the above-mentioned chemical formula, hexadecyl trimethylammonium chloride, tetradecyl trimethylammonium chloride, a DEDOSHIRU trimethylammonium star's picture, a DESHIRU trimethylammonium star's picture, an octyl trimethylammonium star's picture, etc. can be mentioned.

[0053]

[Embodiment of the Invention]

It explains using drawing 1 – drawing 5, and Table 1 about the high density porous body concerning the example of an operation gestalt of operation gestalt 1 this invention, its manufacture approach, and its engine performance. 60% or more of total pore volume is contained in pole diameter within the limits of $-40 - +40\%$ of the pole diameter which the high density porous body of this example has in within the limits whose pole diameter which shows

the greatest peak in a pore-volume-distribution curve is 1-10nm, and shows the greatest peak in the above-mentioned pore-volume-distribution curve, and bulk density is 0.5g/cc or more further.

[0054] And as shown in drawing 1 (a), the high density porous body 1 which fulfills such conditions is constituted when the primary particles 11 of the submicron order which has pore so much gather, is very small, or hardly exists. [of the clearance 10 between these primary particles 11]

[0055] Moreover, in manufacturing the above-mentioned high density porous body 1 concerning this example, mix, the alkoxy silane, the water, and the surfactant which are a raw material are made to react, a silica / surfactant complex is formed, and, subsequently, a surfactant is removed from the above-mentioned silica / surfactant complex. And the H2 O/Si mole ratio in the above-mentioned raw material is within the limits of ten or less.

[0056] Next, lessons is taken for the samples 1 and 2 which are the high density porous bodies 1 concerning this invention, and the comparison samples C1 and C2 which are the conventional meso porous bodies from the approach of carrying out an engine-performance comparison etc., and they are explained. It explains concretely per manufacture approach of the samples 1 and 2 which are the high density porous bodies 1 which start this invention first.

[0057] About 0.1g of Water [3.6g and 2N] hydrochloric acids was added to tetramethoxy silane (TMOS) 15.2g which is alkoxy silane, and it stirred at the room temperature for 1 hour. In the solution obtained by this addition and stirring, dodecyl trimethylammonium star's picture (DDTA) 7.71g which is a surface active agent was added further, and it stirred violently for several minutes in it, and produced and cheated out of viscosity in it at the solution. Furthermore, the obtained solution was left in the well-closed container for two to three days. The transparent and uniform solid-state was obtained by the above. This solid-state is a silica / surfactant complex.

[0058] The above-mentioned silica / surfactant complex were dried, it calcinated in air after that for 550 degrees C and 6 hours, and the surfactant was removed from this silica / surfactant complex. The solid-state obtained by the above-mentioned baking was ground, the screen was used, and step was kept with the particle size of 100-150 micrometers. By the above, the high density porous body of the shape of powder with a particle size of 100-150 micrometers was obtained. This is a high density porous body concerning a sample 1. In addition, the H2 O/Si ratio in the raw material in a sample 1 was 2.

[0059] Moreover, in the above-mentioned manufacture approach, about 0.1g of Water [3.6g and 2N] hydrochloric acids was added to TMOS15.2g, and mixture (DDTA7.71g and H2 O3.6g) was added in the solution obtained by stirring at a room temperature for 1 hour. Other processes are the same as that of the above-mentioned sample 1. The high density porous body obtained by this manufacture approach is a sample 2. And the H2 O/Si ratio in the raw material in a sample 2 was 4.

[0060] Moreover, in the above-mentioned manufacture approach, about 0.1g of Water [3.6g and 2N] hydrochloric acids was added to TMOS15.2g, and mixture (DDTA7.71g and H2 O18g) was added in the solution obtained by stirring at a room temperature for 1 hour. Other processes are the same as that of the above-mentioned sample 1. The meso porous body obtained by this manufacture approach is the comparison sample C1. And the H2 O/Si ratio in the raw material in the comparison sample 1 was 12.

[0061] Moreover, in the above-mentioned manufacture approach, about 0.1g of Water [3.6g and 2N] hydrochloric acids was added to TMOS15.2g, and mixture (DDTA7.71g and H2 O36g) was added in the solution obtained by stirring at a room temperature for 1 hour. Other processes are the same as that of a sample 1. The meso porous body obtained by this manufacture approach is the comparison sample C2. And the H2 O/Si ratio in the raw material in the comparison sample 2 was 22.

[0062] The bulk density and specific surface area of the samples 1 and 2 obtained by the above and the comparison samples C1 and C2 were measured. the above-mentioned bulk density — the weight and the volume of each samples 1 and 2 and the comparison samples C1 and C2 — a weigher and a measuring cylinder — **** — it asked by things. It asked for the above-mentioned specific surface area with the BET one point method for BET method by the automatic specific-surface-area measuring device of Ohkuriken. The above-mentioned measurement result is shown in Table 1.

[0063] According to this table, it turned out that samples 1 and 2 have bulk density higher than the comparison samples C1 and C2. Moreover, it turned out that samples 1 and 2 have a specific surface area higher than the comparison samples C1 and C2. Therefore, it turned out that samples 1 and 2 are excellent in an adsorption property or a catalyst property as compared with the comparison samples C1 and C2. Moreover, since samples 1 and 2 had higher bulk density, it understood that it can be filled up with more amounts compared with the comparison samples C1 and C2 when filling up the restoration container of this volume, and engine performance, such as an adsorption property or a catalyst property, can be made to discover enough.

[0064] Next, the nitrogen adsorption isotherm, the pore-volume-distribution curve, the steam adsorption isotherm, and the powder X diffraction of a sample 1 were measured or calculated, and were shown in drawing 2 - drawing 5 . First, drawing 2 is nitrogen adsorption isotherm. This was measured by the amount method of constant volume in liquid nitrogen temperature. Moreover, drawing 3 is a pore distribution curve. Cranston-Incaly from the nitrogen adsorption isotherm which this showed to drawing 2 — it calculated using law.

[0065] Moreover, drawing 4 is the steam constant-temperature line. This used BELSORP18 made from a Japanese bell, and measured it by the amount method of constant volume in 25 degrees C. Moreover, drawing 5 is a powder X diffraction pattern. This was obtained by scanning in a part for 2 times (2theta)/by making CuKalpha into X line source using physical science RAD-B equipment. In addition, slit width was -0.3mm [per degree] - 1 time.

[0066] From the nitrogen adsorption isotherm of drawing 2 , the sample 1 showed adsorbent [high] from low relative vapor pressure (P/P0), was made into nitrogen gas (STP, standard conditions) by P/P 0= 0.2, and showed the amount of adsorption of 200 cc/g. This value showed that the pore volume of the high density porous body concerning a sample 1 was 0.31 cc/g. Next, the pore-volume-distribution curve of drawing 3 showed that the pole diameter of the high density porous body concerning a sample 1 was 1.5nm.

[0067] By the steam adsorption isotherm of drawing 4 , the sample 1 showed the property that the amount of adsorption changes a lot within the limits of P/P0=0-0.3. The amounts of adsorption of the steam at the time of P/P 0= 0.1 and P/P 0= 0.3 were 0.07 g/g and 0.28 g/g, respectively. By the 0.71g [/cc] high density porous body, if it changes into the amount of adsorption per **, it will be set to cc in 0.05g /and cc and 0.2g /, and the difference will be set to cc in 0.15g /, respectively. That is, a sample 1 serves as a high density porous body of claim 2. And the constant-temperature line by the side of adsorption and desorption was mostly in agreement, and did not show a hysteresis.

[0068] Moreover, the 2nd steam adsorption isotherm (secondary) was measured using the same sample 1. However, adsorption of the 1st steam adsorption isotherm (primary) and a steam since it was isomorphism-like mostly showed that the structure of a sample 1 did not change.

[0069] In the powder X diffraction pattern of drawing 5, a clear peak was not observed in the range whose angle of diffraction is one - 60 degrees. Therefore, it turned out that it does not have the crystal structure with a regular sample 1.

[0070] As mentioned above, although it did not have a sample 1, as for the regular crystal structure, it was found by having the uniform pore centering on 1.5nm, and high bulk density.

[0071]

[Table 1]

(表 1)

	試料No.	H ₂ O/Si モル比	高密度 (g/cc)	比表面積 (m ² /g)
本 発 明	1	2	0.71	1066
	2	4	0.55	1022
比 較 例	C 1	1 2	0.38	850
	C 2	2 2	0.35	765

[0072] In the example 1 of an operation gestalt, the example of two examples of an operation gestalt is the manufacture approach of a different high density porous body, and, in separating the silica / surfactant complex generated in the solution which mixed the raw material, is the manufacture approach which adopted the approach of carrying out the coat of the solution to a substrate.

[0073] About 0.1g of Water [3.6g and 2N] hydrochloric acids was added to TMOS15.2g, and it stirred at the room temperature for 1 hour. In the solution obtained by this addition and stirring, DDTA7.71g was added further, and it stirred violently for several minutes in it, and produced and cheated out of viscosity in it at the solution. Furthermore, the coat of the obtained solution was carried out on the surface of the aluminum plate, and it was left at the room temperature on two to the 3rd. By the above, the uniform transparent membrane was obtained in the front face of the above-mentioned aluminum plate. This transparent membrane is a silica / surfactant complex.

[0074] Then, the silica / surfactant complex which is the above-mentioned transparent membrane were dried, and, subsequently to the inside of air, it calcinated for 550 degrees C and 6 hours. By the above, the high density porous body concerning this invention was obtained. In addition, also in the manufacture approach of this example, the H₂ O/Si ratio in the raw material was 2. Others are the same as that of the example 1 of an operation gestalt.

[0075] The example of three examples of an operation gestalt is explained per engine performance of the samples 3 and 4 manufactured using a different surfactant from the surfactant used for the samples 1 and 2 shown in the example 1 of an operation gestalt. It explains about the manufacture approach of samples 3 and 4. About 0.1g of Water [3.6g and 2N] hydrochloric acids was added to TMOS15.2g, and it stirred at the room temperature for 1 hour. In the solution obtained by this addition and stirring, DESHIRU trimethylammonium star's picture (DTA) 7.01g which is a surface active agent was added further, and it stirred violently for several minutes in it, and produced and cheated out of viscosity in it at the solution. Furthermore, the obtained solution was left in the well-closed container for two to three days. The transparent and uniform solid-state was obtained by the above. This solid-state is a silica / surfactant complex.

[0076] The above-mentioned silica / surfactant complex were dried, it calcinated in air after that for 550 degrees C and 6 hours, and the surfactant was removed from this silica / surfactant complex. The solid-state obtained by the above-mentioned baking was ground, the screen was used, and step was kept with the particle size of 100-150 micrometers. By the above, the high density porous body of the shape of powder with a particle size of 100-150 micrometers was obtained. This is a high density porous body concerning a sample 3. In addition, the H₂ O/Si ratio in the raw material in a sample 3 was 2.

[0077] Moreover, octyl trimethylammonium star's picture (OTA) 6.31g was added as a surface active agent in the solution obtained by the above-mentioned addition and stirring, it processed like the above in it, and the transparent and uniform solid-state was obtained in it. Furthermore, this solid-state was processed like the above and the powder-like high density porous body was obtained. This is a high density porous body concerning a sample 4. In addition, the H₂ O/Si ratio in the raw material in a sample 4 was 2.

[0078] And bulk density and specific surface area were measured by the same approach as the example 1 of an operation gestalt a sample 3 and per four. This result was shown in Table 2. According to this table, as a surfactant, when DTA and OTA were used, the high density porous body which was excellent like the example 1 of an operation gestalt was able to be obtained.

[0079]

[Table 2]

(表 2)

試料No	界面活性剤	嵩密度 (g/cc)	比表面積 (m^2/g)
3	D T A	0.66	712
4	O T A	0.65	650

DTA… デシルトリメチルアンモニウムブロマイド
 OTA… オクチルトリメチルアンモニウムブロマイド

[0080] The example of four examples of an operation gestalt is the adsorption heat pump which used the high density porous body concerning this invention as an adsorbent, as shown in drawing 6. In addition, although this example is a direct-vent-system adsorption pump, the high density porous body of this invention can be used as an adsorbent also in release type adsorption heat pump.

[0081] Next, the direct-vent-system adsorption heat pump 2 of this example is explained. The above-mentioned adsorption heat pump 2 consists of piping 25, 27, and 28 and the bulb 26 which connect mutually an adsorber 21, an evaporator 22, a condenser 23, and these, as shown in drawing 6. And the adsorbate circulates through between these.

[0082] By switching the above-mentioned piping, the above-mentioned adsorbate faces to an adsorber 21 through the adsorption (Ads.) piping 28 in the state of a steam from an evaporator 22. Then, the above-mentioned adsorbate passes along the desorption (Des.) piping 25 from the above-mentioned adsorber 21, and circulates to a condenser 23. Furthermore, the above-mentioned adsorbate is again returned to an evaporator 22 via piping 27 from the above-mentioned condenser 23 after that. In addition, the piping 210,220,230 for heat exchange is formed in the interior of the above-mentioned adsorber 21, an evaporator 22, and a condenser 23.

[0083] And the temperature of an adsorbent is made to go up and down according to the low temperature of temperature T_a and T_{reg} ($T_a < T_{reg}$), and two hot heat sources. This repeats the cycle through which it circulates from adsorption to desorption. In addition, cold energy (T_{cold}) can obtain warm temperature (T_h) by swerving, swerving and taking out a heat of adsorption [in / for endoergic / in an evaporator 22 / an adsorber 21].

[0084] The adsorbent which consists of a high density porous body concerning this invention is installed in the interior of the above-mentioned adsorber 21 in the above-mentioned adsorption heat pump. Inside the above-mentioned adsorber 21, in order to make easy heat exchange between the above-mentioned adsorbent and a heat carrier, it arranges so that many metal fins may lap. The above-mentioned adsorbent can be made granular and the clearance between the above-mentioned metal fin and a metal fin can be filled up with it. Moreover, a coat can also be carried out to the front face of the above-mentioned metal fin.

[0085] In addition, when carrying out the coat of the above-mentioned adsorbent to especially the above-mentioned metal fin, the coat of the adsorbent may be carried out to it to the metal fin simple substance before attachment by the adsorber 21, respectively. Moreover, after assembling an adsorber 21, the coat of the above-mentioned adsorbent can also be carried out to the metal fin of the interior.

[0086] Since the high density porous body concerning this invention is used as an adsorbent according to this example, the effectiveness that high refrigerating capacity is discovered by use of a little adsorbent can be acquired.

[0087]

[Effect of the Invention] In case bulk density is high, has a uniform pore diameter and uses it as an adsorbent or a catalyst like the above according to this invention, the high density porous body which can discover the property enough, and its manufacture approach can be offered.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention] This invention relates to a high density porous body usable as a catalyst which can be used for the adsorbent which can be used for recovery of a solvent, a gasoline, etc., adsorption heat pump, temperature control, water treatment, deodorization, etc., reforming, cracking of purification of exhaust gas, organic synthesis, and petroleum, etc., and its manufacture approach.

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PRIOR ART

[Description of the Prior Art] The porous body which is in the range especially whose pore diameter (the diameter of pore is meant in this specification.) is 1-10nm in a porous body, and is distributed over the range where the above-mentioned pore diameter is especially narrow is called a meso porous body. There is the approach of making a surfactant act on stratified silicate and manufacturing as the manufacture approach of the above-mentioned meso porous body, for example (JP,4-238810,A, JP,6-24867,A). Moreover, there is also a method of making a silica and Si alkoxide react with a surfactant, and manufacturing them (JP,5-503499,A).

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EFFECT OF THE INVENTION

[Effect of the Invention] In case bulk density is high, has a uniform pore diameter and uses it as an adsorbent or a catalyst like the above according to this invention, the high density porous body which can discover the property enough, and its manufacture approach can be offered.

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TECHNICAL PROBLEM

[Problem(s) to be Solved] However, by the conventional manufacture approach, only the small meso porous body of bulk density was able to be manufactured. Therefore, when these meso porous bodies were used as an adsorbent or a catalyst, the restoration container for holding an adsorbent or a catalyst etc. was able to be filled up only with the comparatively little meso porous body. In this case, the engine performance of the above-mentioned meso porous body was not able to be made to discover enough.

[0004] Moreover, in order to make the engine performance of the above-mentioned meso porous body discover enough, enlarging the restoration container filled up with this meso porous body is also considered. However, the problem that the equipment (for example, adsorption heat pump) which contains this restoration container etc. will be enlarged because a restoration container etc. becomes large had arisen.

[0005] In case bulk density is high, has a uniform pore diameter and uses this invention as an adsorbent or a catalyst in view of this trouble, it tends to offer the high density porous body which can discover the property enough, and its manufacture approach.

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MEANS

[Means for Solving the Problem] 60% or more of total pore volume is contained in pole diameter within the limits of -40 – $+40\%$ of the pole diameter which is in within the limits whose pole diameter which shows the greatest peak in a pore-volume-distribution curve is $1-10\text{nm}$, and shows the greatest peak in the above-mentioned pore-volume-distribution curve, and the high density porous body further characterized by bulk density being 0.5g/cc or more has invention of claim 1.

[0007] It explains below about an operation of this invention. The high density porous body of this invention has the above-mentioned description in the pore-volume-distribution curve mentioned later. Moreover, the bulk density is within the limits of specification. As the high density porous body which fulfills such conditions is shown in below-mentioned drawing 1 (a), it is constituted when the primary particles of the submicron order which has pore so much gather, and the clearance between these primary particles is very small, or hardly exists.

[0008] On the other hand, the meso porous body with the conventional low bulk density mentioned above has the structure which had a big clearance among the primary particles of the same submicron order as the above, as shown in drawing 1 (b). An adsorption property or a catalyst property peculiar to the above-mentioned meso porous body etc. is mainly discovered by the pore inside a primary particle. The high density porous body of this invention has a very small clearance between the primary particles which are unrelated to the manifestation of an adsorption property or a catalyst property, or has the structure which hardly exists. For this reason, high structure of bulk density can be realized in the high density porous body of this invention, without spoiling an adsorption property or a catalyst property.

[0009] As mentioned above, in case according to this invention bulk density is high, has a uniform pole diameter and uses it as an adsorbent or a catalyst, the high density porous body which can discover the property enough can be obtained.

[0010] Moreover, the above is further explained to a detail. First, generally in the adsorption isotherm of the steam in a meso porous body, it is known that adsorption/desorption of a steam will occur [relative vapor pressure (P/P_0)] rapidly in $0.1-0.81$. And it can be drawn from the relation of the pole diameter and relative vapor pressure in the Kelvin equation whether the adsorption isotherm of a certain specific meso porous body fulfills the above-mentioned conditions.

[0011] The Kelvin equation is a formula showing the relation between the pore radius (r) of a meso porous body, and the relative vapor pressure (P/P_0) from which an adsorbate starts capillary condensation, and the following (1) types can show here.

$$\ln(P/P_0) = (2VL\gamma\cos\theta)/(rRT) \dots (1)$$

In addition, for molar volume when Above VL has a liquid adsorbate, and γ , surface tension when an adsorbate is liquid, and θ are [a gas constant and T of a contact angle and R] absolute temperature.

[0012] When an adsorbate is a steam, the numeric value of $VL=18.05$ and $10^{-6}\text{m}^3/\text{mol}$, $\gamma=72.59$ and 10^{-3}N/m , $R=8.3143\text{ J/deg-mol}$, and $\theta=0$ can be substituted here at (1) type. Consequently, the above-mentioned (1) formula is $\ln(P/P_0) = -1.058/r$ used as the following (2) types... (2)

In addition, the unit of r is nm.

[0013] The above-mentioned (2) formula shows generating in the range of P/P_0 with narrower adsorption/desorption of a steam, when distributed over the range where a pole diameter is more narrow in pore volume distribution. That is, the difference of P/P_0 in adsorption isotherm adsorption starts P/P , and P/P_0 to which adsorption reached saturation is small.

[0014] It is in within the limits the pole diameter of whose is $1-10\text{nm}$ in the high density porous body of this invention. And when a pole diameter is in the range which is $1-10\text{nm}$ from the above-mentioned (2) formula, it turns out that the range of P/P_0 which starts adsorption/desorption of the steam in adsorption isotherm is set to $0.12-0.81$. This range is range which adsorption/desorption of a steam produce rapidly, as mentioned above. Thereby, it turns out that it has the property that the amount of adsorption changes a lot by the change of small P/P_0 with the high density porous body (P/P_0 setting in the range of $0.12-0.81$) of this invention optimal as an adsorbent in adsorption heat pump, a thermoregulator, etc.

[0015] In addition, it explains below per above-mentioned pore distribution curve. The above-mentioned pore-volume-distribution curve shows the curve which plotted the value (dV/dD) which differentiated the pore volume (V) of a meso porous body with the pole diameter (D) to the pole diameter (D) (refer to drawing 3). The above-mentioned pore-volume-distribution curve can be created by the gas adsorption method shown below. In addition, the gas best used in the describing [above] gas adsorption method is nitrogen.

[0016] First, at liquid nitrogen temperature (-196 degrees C), nitrogen gas is introduced and the target meso porous body is asked for the amount of adsorption in the amount method of constant volume, or a weight method. Then, the pressure of the nitrogen gas to introduce is made to increase gradually, and adsorption isotherm is created by plotting the amount of adsorption of nitrogen gas to each equilibrium pressure. Cranston-Inclay from this adsorption isotherm -- law and Pollimore-Heal -- drawing the above-mentioned pore-volume-distribution curve using the calculus of law -- things are made.

[0017] Next, the expression in above-mentioned claim 1 "60% or more of total pore volume is contained in the diameter range of $\pm 40\%$ of the diameter which shows the greatest peak in the above-mentioned pore-volume-distribution curve" is expressing the following conditions. For example, the meso porous body alpha from which the greatest peak in

the pore-volume-distribution curve mentioned above is set to 2.7nm is assumed. It asks for the pore volume V which summed up the volume of the pore which has a pole diameter in the range of $1.62 (= 2.7 \times 0.6) - 3.78 (= 2.7 \times 1.4)$ nm in this meso porous body alpha. On the other hand, in the above-mentioned meso porous body alpha, the grand total V_{all} of total pore volume is searched for.

[0018] And when the value of V/V_{all} is more than 0.6 (60%) temporarily, it can be said that it is one of the high density porous bodies which require the above-mentioned meso porous body alpha for this invention. Or in the pore-volume-distribution curve of the above-mentioned meso porous body alpha, also when the integral value of the range where a pole diameter becomes 1.62-3.78nm is 60% or more of a total integral area of a pore-volume-distribution curve, it can be said that the above-mentioned meso porous body alpha is a high density porous body concerning this invention.

[0019] Since the high density porous body of this invention which fulfills such conditions is distributed over the range where a pole diameter is narrow, it can acquire the effectiveness that the amount of adsorption changes a lot, to change of small P/P₀. In addition, when contained less than 60% of total pore volume, the amount-of-adsorption change to change of P/P₀ is small in the diameter range of $\pm 40\%$ of the diameter which shows the greatest peak in the above-mentioned pore-volume-distribution curve, and a possibility that neither a gas conditioning function nor an adsorption heat pump property may be discovered enough is in it.

[0020] Moreover, the bulk density of the high density porous body of this invention is 0.5g/cc or more. For this reason, in case the above-mentioned high density porous body is used as an adsorbent or a catalyst, a restoration container can be filled up with a lot of high density porous bodies as compared with the former. The manifestation of a thereby more high adsorption property or a catalyst property is attained. Or it becomes possible to make small the restoration container of a high density porous body etc., and the equipment which sets this restoration container etc. can be made small.

[0021] In addition, when the above-mentioned bulk density is less than 0.5g/cc, in order to be able to fill up a restoration container etc. only with a little high density porous body, and not to fully discover a required property or to secure a required property, there is a possibility that it is necessary to enlarge a restoration container, and equipment may be enlarged, for example, mount may become difficult.

[0022] As mentioned above, it turns out that the high density porous body of this invention has the outstanding effectiveness like the above so that it may be known.

[0023] Next, it is desirable that amount-of-adsorption change when it is in within the limits whose pole diameter which shows the greatest peak in a pore-volume-distribution curve is 1-10nm like invention of claim 2 and relative vapor pressure changes 0.2 times in steam adsorption isotherm has a part 0.1g [/cc] or more. The effectiveness that humidity control and an adsorption heat pump property are discovered by the thereby more little porous body can be acquired. In addition, when the above-mentioned amount-of-adsorption change is less than 0.1g/cc, a lot of porous bodies are needed, and there is a possibility of producing the problem that a restoration container and the whole equipment are enlarged.

[0024] With in addition, the above "amount-of-adsorption change when relative vapor pressure changes 0.2 times has a part 0.1g [/cc] or more" When it presupposes that the amounts of adsorption in case relative vapor pressure (P/P₀) is 0.1 and 0.3 are V_{0.1} = 0.2g/cc and V_{0.3} = 0.5g/cc, respectively in steam adsorption isotherm, It is the semantics of amount-of-adsorption change when relative vapor pressure changes 0.2 times being set to V_{0.3}-V_{0.1} = 0.3g/cc, and corresponding in "0.1g/cc or more." Change of relative vapor pressure may be good even in the range of 0 - 1 throat, and amount-of-adsorption change may be [a part 0.1g /cc / or more] a part of high density porous body.

[0025] Next, it is desirable to have one or more peaks in whenever [angle-of-diffraction / which is in within the limits whose pole diameter which shows the greatest peak in a pore-volume-distribution curve is 1-10nm like invention of claim 3, and is equivalent to d value of 1nm or more within the limits in a powder X diffraction pattern]. This shows that the periodic crystal structure 1nm or more exists in a high density porous body, and is in the range whose pole diameter is 1-10nm, and shows that it is distribution with a uniform pole diameter. It turns out that it has the property which was excellent within the limits of P/P₀ with a narrow steam etc. by this as the adsorption heat pump of causing ** and desorption, or a gas conditioning agent.

[0026] Next, as for the above-mentioned high density porous body, it is desirable like invention of claim 4 that more than 80wt% of the whole consists of silicon and oxygen. Thereby, association with an admolecule (for example, water molecule) and a porous body front face will become comparatively weak, and the molecule to which it stuck tends comparatively] to ****, and it can repeat ** and desorption reversibly. In addition, when the content of silicon and oxygen is less than [80wt%], by mixing a different element from silicon and oxygen, solid acid nature etc. is discovered by the front face and there is a possibility that an admolecule may not **** easily.

[0027] Next, invention of claim 5 is mixed, makes the alkoxysilane, the water, and the surfactant which are a raw material react, forms a silica / surfactant complex, and is in the manufacture approach of the high density porous body characterized by the H₂ O/Si mole ratio in the above-mentioned raw material being ten or less in the approach of subsequently manufacturing a high density porous body by removing a surfactant from the above-mentioned silica / surfactant complex.

[0028] The above "the H₂ O/Si mole ratio in a raw material" shows the ratio of the total amount of Si contained in other raw materials to the total amount of added H₂ O in mixing of the above-mentioned raw material. When the above "an H₂ O/Si mole ratio" is ten or less shows that the consistency of the manufactured porous body can be raised. In addition, the above "an H₂ O/Si mole ratio" becomes [alkoxysilane / the clearance between the particles of the generated silica which carries out hydrolysis and condensation] large in being larger than 10, and there is a possibility that the consistency of the generated silica may fall, as a result. Therefore, there is a possibility that it may become impossible to obtain a high density porous body.

[0029] Moreover, as for the minimum of the above "an H₂ O/Si mole ratio", it is desirable that it is one or more. When the above-mentioned value is less than one, hydrolysis of alkoxysilane does not take place but there is a possibility that a silica may not be obtained as a result. Therefore, there is a possibility that it may become impossible to obtain a high density porous body.

[0030] Next, it is desirable to add a surfactant, after adding water to alkoxysilane first and stirring at a room temperature especially as the mixed approach of the above-mentioned raw material for 10 minutes to 3 hours, although not limited. Moreover, as for the above-mentioned water, it is desirable that 0.5-10 mols add to one mol of silicon which the above-mentioned alkoxysilane contains. When alkoxysilane condenses slowly through a straight chain-like

alkoxysilane polymerization object by this mixed approach, the organization of a precise silica is formed and the effectiveness that a consistency increases can be acquired.

[0031] When the addition of the above-mentioned water is less than 0.5 mols, hydrolyzing [of alkoxysilane] becomes inadequate, the frame of a firm high density porous body is not formed, or there is a possibility that the consistency of a porous body may fall. On the other hand, when it adds more mostly than ten mols, hydrolysis and condensation of alkoxysilane are performed quickly and there is a possibility that the consistency of a rough next door high density porous body may fall [a silica organization].

[0032] Moreover, when the above-mentioned mixing time is less than 10 minutes, there is a possibility that the consistency of a high density porous body may fall. On the other hand, when 3 hours is exceeded, there is a possibility that uniform pore may not be formed.

[0033] Furthermore, it is desirable to add a small amount of acid as a pH regulator in the case of the above-mentioned mixing. Thereby, it becomes easy to dissolve each component and becomes easy to prepare a uniform solution. And as for pH in the case of the above-mentioned mixing, it is desirable to be adjusted to the range of 1-4. When Above pH is less than one, hydrolysis and condensation advance quickly and there is a possibility that formation of uniform pore may be barred. Or there is a possibility that the consistency of the generated porous body may fall. On the other hand, when Above pH is larger than 4, the dissolution of each component is inadequate and there is a possibility that required hydrolysis may not be performed. Moreover, as the above-mentioned acid, although dilute hydrochloric acid (for example, two conventions) can be used, other acids, such as a sulfuric acid, are sufficient.

[0034] Moreover, it may be made to dissolve in little water and the above-mentioned surfactant may be added, although you may add with powder. And as for the addition of the above-mentioned surfactant, it is desirable to add to one mol of Si contained in [all] a raw material, so that it may become 1-10 mols. When there are more additions of the above-mentioned surfactant than ten mols, the excessive surfactant which is not contributed to formation of the above-mentioned silica / surfactant complex is intermingled in the above-mentioned silica / surfactant complex, and or the consistency of a high density porous body falls, there is a possibility that a manufacturing cost may become high.

[0035] On the other hand, when the above-mentioned addition is less than one mol, the silica of the surplus which does not contribute to formation of the above-mentioned silica / surfactant complex is intermingled in the above-mentioned silica / surfactant complex, the ratio of the part in which uniform pore is formed falls, and there is a possibility that a required function may not be discovered enough. Furthermore, the above-mentioned silica forms a thick layer in the front face of a silica/surfactant, and adheres to it, and there is also a possibility that the pore volume of the high density porous body obtained by this may decrease.

[0036] Subsequently, a surfactant is removed from the above-mentioned silica / surfactant complex, and it is explained as a high density porous body per [to make] approach. That is, although the above-mentioned silica / surfactant complex are generated in the solution which mixed the raw material, first of all, a silica / surfactant complex is separated out of this solution. Then, a surfactant is removed from obtained independent silica / surfactant complex, and it makes with a high density porous body. It explains below about these processes.

[0037] First, the solution containing a silica/surfactant is solidified while the whole solution had maintained the uniform condition gradually, when it was left as it is. Therefore, the above-mentioned solution becomes massive by leaving the above-mentioned solution in a well-closed container or an open container. It grinds, after drying the lump obtained by this. Furthermore, after that, it applies to a screen and the particle size of a grinding object is arranged. Thereby, the silica / surfactant complex of the shape of powder which has a desired particle size can be obtained.

[0038] Moreover, on the substrate which consists of aluminum etc., the coat of the above-mentioned solution is carried out, and it is left. Thereby, it can solidify on a substrate and the above-mentioned solution can obtain film-like a silica / surfactant complex. In addition, as an approach of carrying out the coat of the solution to the above-mentioned substrate, a spin coat method, the casting method, a dip coating method, etc. can mention.

[0039] next, the above -- a surfactant is removed from the silica / surfactant complex of the shape of powdered or film, and it makes with a high density porous body. As this removal approach, the approach by baking and the approach of using a solvent mention, and it is *****, for example. First, the removal approach by baking is shown. The above-mentioned silica / surfactant complex are preferably heated in 500 degrees C - 700 degrees C in 400 degrees C - 1000 degrees C. The above-mentioned heating time can remove a surfactant to extent which does not interfere on 30 minutes or more, then practical use. However, in order to remove the above-mentioned surfactant completely, heating for 1 hour or more is more desirable than the above-mentioned silica / surfactant complex.

[0040] Moreover, since temperature is too low when whenever [above-mentioned stoving temperature] is less than 400 degrees C, there is a possibility that combustion removal of the surfactant cannot fully be carried out. Moreover, since temperature is too high when whenever [above-mentioned stoving temperature] exceeds 1000 degrees C, there is a possibility that pore structure may collapse. In addition, the ambient atmosphere which is in charge of the above-mentioned heating should just circulate air. However, since a lot of combustion gas occurs, it is more desirable to circulate inert gas, such as nitrogen gas, the early stages of heating.

[0041] Next, the removal approach which uses a solvent is shown. First, the solvent which added the little cation component to the solvent with large solubility to a surfactant is created. The above-mentioned solvent is made to distribute the above-mentioned silica / surfactant complex, and it stirs. Thereby, a surfactant dissolves and dissociates from the above-mentioned silica / surfactant complex into a solvent. Then, solid content is collected from the above-mentioned solvent. It is the high density porous body for which the above-mentioned solid content asks.

[0042] As the above-mentioned solvent, alcohol, such as ethanol and a methanol, an acetone, etc. can be used, for example. Moreover, in order to add the above-mentioned cation component to a solvent, it is desirable to add the following matter to this solvent. As the above-mentioned matter, a hydrochloric acid, an acetic acid, a sodium chloride, potassium chloride, etc. can be used. The above-mentioned surfactant can be separated from the above-mentioned silica / surfactant complex thereby much more efficiently.

[0043] And as for the addition concentration of the above-mentioned cation, it is desirable to carry out in 0.1-10 mols/l. to the above-mentioned solvent. When the above-mentioned addition concentration is less than 0.1 mols/l., separation of a surfactant is inadequate and there is a possibility that a surfactant may remain in a high density porous body. On the other hand, when the above-mentioned addition concentration is larger than 1. ten mols /, there is a possibility of there being no effectiveness added more than it, and becoming cost quantity. Moreover, there is a possibility that the silica frame of a high density porous body may collapse.

[0044] Next, as for the variance of a silica / surfactant complex to the above-mentioned solvent, it is desirable that

they are 0.5–50g to 100 cc of solvents. In being less than 0.5g, the processing effectiveness of a silica / surfactant complex is bad, and there is a possibility that the cost and the manufacturing cost of a solvent may be applied. On the other hand, in [than 50g] more, separation of a surfactant is inadequate and there is a possibility that a surfactant may remain in a high density porous body.

[0045] Moreover, it is desirable to perform stirring after making the above-mentioned solvent distribute a silica / surfactant complex in a 25–100-degree C temperature requirement. Thereby, the processing time can be shortened for separation of a surfactant. When the above-mentioned temperature is less than 25 degrees C, there is a possibility that compaction of the processing time may not be expected. On the other hand, when 100 degrees C is exceeded, the energy cost for heating starts or there is a possibility that the loss by volatilization of a solvent may increase.

[0046] In addition, the above-mentioned high density porous body can be used as powder, and can be screened and fabricated in the configuration according to the purpose of use for every particle size of the. And the process of these sieving and shaping can be performed before the process which removes the above-mentioned surfactant. In this case, collapse of the pore at the time of shaping is barred, or the effectiveness that shaping reinforcement improves can be acquired. Moreover, after fabricating the above-mentioned silica/surfactant in the configuration finally demanded, a surfactant can be removed and it can also consider as a high density porous body. In this case, collapse of the pore at the time of shaping can be prevented. Moreover, shaping reinforcement can be raised.

[0047] Next, as alkoxysilane in the above-mentioned raw material, alkyl alkoxysilane, such as a tetramethoxy silane, a tetra-ethoxy silane, tetra-propoxysilane, or methyl trimetoxysilane, etc. can be used. One kind or two kinds or more of such combination is sufficient.

[0048] And as for especially the above-mentioned alkoxysilane, according to invention of claim 6, it is desirable that it is a tetramethoxy silane. A high density porous body can be manufactured thereby comparatively easily.

[0049] Moreover, as for the above-mentioned surfactant, it is desirable like invention of claim 7 that it is the compound which has a long-chain alkyl group and a hydrophilic group. By using this compound, the effectiveness that the molecular assembly of a surfactant is formed in a reaction solution, and the 1–10nm uniform pore corresponding to the magnitude of that molecular assembly is formed in a high density porous body can be acquired.

[0050] Moreover, as the above-mentioned alkyl group, the thing of 2–18 has a desirable carbon atomic number. By using the surfactant which consists of these alkyl groups, the effectiveness that the above-mentioned molecular assembly is formed efficiently can be acquired. In addition, when there are more above-mentioned carbon atomic numbers than 18, such a surfactant is not marketed but has a possibility that cost may start. Moreover, when a carbon atomic number is 1 (i.e., when the above-mentioned alkyl group is a methyl group), there is a possibility that the above-mentioned molecular assembly may be hard to be formed, and 1–10nm uniform pore may not be formed. Moreover, as the above-mentioned hydrophilic group, $-N+3(CH_3)$, $=N+2(CH_3)$, $**N+**(CH_3)N^+$, $-NH_2$, $-NO$, $-OH$, $-COOH$, etc. are mentioned, for example.

[0051] Next, as the above-mentioned surfactant, the compound shown in the following chemical formulas can be used. Moreover, it is desirable like invention of claim 8 as such a compound to use alkyl trimethylammonium.

$C_n H_{2n+1}-N(CH_3)_3 X$ — n is the integer of 2–18 and X is halogenide ion, such as chloride ion and bromide ion, here.

[0052] By using such a surfactant, the effectiveness that the molecular assembly of a surfactant is efficiently formed in a reaction solution, and the 1–10nm uniform pore corresponding to the molecular assembly is easy to be formed can be acquired. In addition, as an example of a surface active agent with the above-mentioned chemical formula, hexadecyl trimethylammonium chloride, tetradecyl trimethylammonium chloride, a DEDOSHIRU trimethylammonium star's picture, a DESHIRU trimethylammonium star's picture, an octyl trimethylammonium star's picture, etc. can be mentioned.

[0053]

[Embodiment of the Invention]

It explains using drawing 1 – drawing 5, and Table 1 about the high density porous body concerning the example of an operation gestalt of example of operation gestalt 1 this invention, its manufacture approach, and its engine performance. 60% or more of total pore volume is contained in pole diameter within the limits of $-40 - +40\%$ of the pole diameter which the high density porous body of this example has in within the limits whose pole diameter which shows the greatest peak in a pore-volume-distribution curve is 1–10nm, and shows the greatest peak in the above-mentioned pore-volume-distribution curve, and bulk density is 0.5g/cc or more further.

[0054] And as shown in drawing 1 (a), the high density porous body 1 which fulfills such conditions is constituted when the primary particles 11 of the submicron order which has pore so much gather, is very small, or hardly exists. [of the clearance 10 between these primary particles 11]

[0055] Moreover, in manufacturing the above-mentioned high density porous body 1 concerning this example, mix, the alkoxysilane, the water, and the surfactant which are a raw material are made to react, a silica / surfactant complex is formed, and, subsequently, a surfactant is removed from the above-mentioned silica / surfactant complex. And the H2 O/Si mole ratio in the above-mentioned raw material is within the limits of ten or less.

[0056] Next, lessons is taken for the samples 1 and 2 which are the high density porous bodies 1 concerning this invention, and the comparison samples C1 and C2 which are the conventional meso porous bodies from the approach of carrying out an engine-performance comparison etc., and they are explained. It explains concretely per manufacture approach of the samples 1 and 2 which are the high density porous bodies 1 which start this invention first.

[0057] About 0.1g of Water [3.6g and 2N] hydrochloric acids was added to tetramethoxy silane (TMOS) 15.2g which is alkoxysilane, and it stirred at the room temperature for 1 hour. In the solution obtained by this addition and stirring, dodecyl trimethylammonium star's picture (DDTA) 7.71g which is a surface active agent was added further, and it stirred violently for several minutes in it, and produced and cheated out of viscosity in it at the solution. Furthermore, the obtained solution was left in the well-closed container for two to three days. The transparent and uniform solid-state was obtained by the above. This solid-state is a silica / surfactant complex.

[0058] The above-mentioned silica / surfactant complex were dried, it calcinated in air after that for 550 degrees C and 6 hours, and the surfactant was removed from this silica / surfactant complex. The solid-state obtained by the above-mentioned baking was ground, the screen was used, and step was kept with the particle size of 100–150 micrometers. By the above, the high density porous body of the shape of powder with a particle size of 100–150 micrometers was obtained. This is a high density porous body concerning a sample 1. In addition, the H2 O/Si ratio in the raw material in a sample 1 was 2.

[0059] Moreover, in the above-mentioned manufacture approach, about 0.1g of Water [3.6g and 2N] hydrochloric acids was added to TMOS15.2g, and mixture (DDTA7.71g and H2 O3.6g) was added in the solution obtained by stirring

at a room temperature for 1 hour. Other processes are the same as that of the above-mentioned sample 1. The high density porous body obtained by this manufacture approach is a sample 2. And the H₂O/Si ratio in the raw material in a sample 2 was 4.

[0060] Moreover, in the above-mentioned manufacture approach, about 0.1g of Water [3.6g and 2N] hydrochloric acids was added to TMOS15.2g, and mixture (DDTA7.71g and H₂O18g) was added in the solution obtained by stirring at a room temperature for 1 hour. Other processes are the same as that of the above-mentioned sample 1. The meso porous body obtained by this manufacture approach is the comparison sample C1. And the H₂O/Si ratio in the raw material in the comparison sample 1 was 12.

[0061] Moreover, in the above-mentioned manufacture approach, about 0.1g of Water [3.6g and 2N] hydrochloric acids was added to TMOS15.2g, and mixture (DDTA7.71g and H₂O36g) was added in the solution obtained by stirring at a room temperature for 1 hour. Other processes are the same as that of a sample 1. The meso porous body obtained by this manufacture approach is the comparison sample C2. And the H₂O/Si ratio in the raw material in the comparison sample 2 was 22.

[0062] The bulk density and specific surface area of the samples 1 and 2 obtained by the above and the comparison samples C1 and C2 were measured. the above-mentioned bulk density — the weight and the volume of each samples 1 and 2 and the comparison samples C1 and C2 — a weigher and a measuring cylinder — **** — it asked by things. It asked for the above-mentioned specific surface area with the BET one point method for BET method by the automatic specific-surface-area measuring device of Ohkuriken. The above-mentioned measurement result is shown in Table 1.

[0063] According to this table, it turned out that samples 1 and 2 have bulk density higher than the comparison samples C1 and C2. Moreover, it turned out that samples 1 and 2 have a specific surface area higher than the comparison samples C1 and C2. Therefore, it turned out that samples 1 and 2 are excellent in an adsorption property or a catalyst property as compared with the comparison samples C1 and C2. Moreover, since samples 1 and 2 had higher bulk density, it understood that it can be filled up with more amounts compared with the comparison samples C1 and C2 when filling up the restoration container of this volume, and engine performance, such as an adsorption property or a catalyst property, can be made to discover enough.

[0064] Next, the nitrogen adsorption isotherm, the pore-volume-distribution curve, the steam adsorption isotherm, and the powder X diffraction of a sample 1 were measured or calculated, and were shown in drawing 2 — drawing 5 . First, drawing 2 is nitrogen adsorption isotherm. This was measured by the amount method of constant volume in liquid nitrogen temperature. Moreover, drawing 3 is a pore distribution curve. Cranston-Incaly from the nitrogen adsorption isotherm which this showed to drawing 2 — it calculated using law.

[0065] Moreover, drawing 4 is the steam constant-temperature line. This used BELSORP18 made from a Japanese bell, and measured it by the amount method of constant volume in 25 degrees C. Moreover, drawing 5 is a powder X diffraction pattern. This was obtained by scanning in a part for 2 times (2theta)/by making CuKalpha into X line source using physical science RAD-B equipment. In addition, slit width was -0.3mm [per degree] - 1 time.

[0066] From the nitrogen adsorption isotherm of drawing 2 , the sample 1 showed adsorbent [high] from low relative vapor pressure (P/P₀), was made into nitrogen gas (STP, standard conditions) by P/P₀= 0.2, and showed the amount of adsorption of 200 cc/g. This value showed that the pore volume of the high density porous body concerning a sample 1 was 0.31 cc/g. Next, the pore-volume-distribution curve of drawing 3 showed that the pole diameter of the high density porous body concerning a sample 1 was 1.5nm.

[0067] By the steam adsorption isotherm of drawing 4 , the sample 1 showed the property that the amount of adsorption changes a lot within the limits of P/P₀=0-0.3. The amounts of adsorption of the steam at the time of P/P₀= 0.1 and P/P₀= 0.3 were 0.07 g/g and 0.28 g/g, respectively. By the 0.71g [/cc] high density porous body, if it changes into the amount of adsorption per **, it will be set to cc in 0.05g /and cc and 0.2g /, and the difference will be set to cc in 0.15g /, respectively. That is, a sample 1 serves as a high density porous body of claim 2. And the constant-temperature line by the side of adsorption and desorption was mostly in agreement, and did not show a hysteresis.

[0068] Moreover, the 2nd steam adsorption isotherm (secondary) was measured using the same sample 1. However, adsorption of the 1st steam adsorption isotherm (primary) and a steam since it was isomorphism-like mostly showed that the structure of a sample 1 did not change.

[0069] In the powder X diffraction pattern of drawing 5 , a clear peak was not observed in the range whose angle of diffraction is one - 60 degrees. Therefore, it turned out that it does not have the crystal structure with a regular sample 1.

[0070] As mentioned above, although it did not have a sample 1, as for the regular crystal structure, it was found by having the uniform pore centering on 1.5nm, and high bulk density.

[0071]

[Table 1]

(表 1)

	試料No.	H ₂ O/Si モル比	高密度 (g/cc)	比表面積 (m ² /g)
本 発 明	1	2	0.71	1066
	2	4	0.55	1022
比 較 例	C 1	1 2	0.38	950
	C 2	2 2	0.35	765

[0072] In the example 1 of an operation gestalt, the example of two examples of an operation gestalt is the manufacture approach of a different high density porous body, and, in separating the silica / surfactant complex generated in the solution which mixed the raw material, is the manufacture approach which adopted the approach of carrying out the coat of the solution to a substrate.

[0073] About 0.1g of Water [3.6g and 2N] hydrochloric acids was added to TMOS15.2g, and it stirred at the room temperature for 1 hour. In the solution obtained by this addition and stirring, DDTA7.71g was added further, and it stirred violently for several minutes in it, and produced and cheated out of viscosity in it at the solution. Furthermore, the coat of the obtained solution was carried out on the surface of the aluminum plate, and it was left at the room temperature on two to the 3rd. By the above, the uniform transparent membrane was obtained in the front face of the above-mentioned aluminum plate. This transparent membrane is a silica / surfactant complex.

[0074] Then, the silica / surfactant complex which is the above-mentioned transparent membrane were dried, and, subsequently to the inside of air, it calcinated for 550 degrees C and 6 hours. By the above, the high density porous body concerning this invention was obtained. In addition, also in the manufacture approach of this example, the H₂ O/Si ratio in the raw material was 2. Others are the same as that of the example 1 of an operation gestalt.

[0075] The example of three examples of an operation gestalt is explained per engine performance of the samples 3 and 4 manufactured using a different surfactant from the surfactant used for the samples 1 and 2 shown in the example 1 of an operation gestalt. It explains about the manufacture approach of samples 3 and 4. About 0.1g of Water [3.6g and 2N] hydrochloric acids was added to TMOS15.2g, and it stirred at the room temperature for 1 hour. In the solution obtained by this addition and stirring, DESHIRU trimethylammonium star's picture (DTA) 7.01g which is a surface active agent was added further, and it stirred violently for several minutes in it, and produced and cheated out of viscosity in it at the solution. Furthermore, the obtained solution was left in the well-closed container for two to three days. The transparent and uniform solid-state was obtained by the above. This solid-state is a silica / surfactant complex.

[0076] The above-mentioned silica / surfactant complex were dried, it calcinated in air after that for 550 degrees C and 6 hours, and the surfactant was removed from this silica / surfactant complex. The solid-state obtained by the above-mentioned baking was ground, the screen was used, and step was kept with the particle size of 100-150 micrometers. By the above, the high density porous body of the shape of powder with a particle size of 100-150 micrometers was obtained. This is a high density porous body concerning a sample 3. In addition, the H₂ O/Si ratio in the raw material in a sample 3 was 2.

[0077] Moreover, octyl trimethylammonium star's picture (OTA) 6.31g was added as a surface active agent in the solution obtained by the above-mentioned addition and stirring, it processed like the above in it, and the transparent and uniform solid-state was obtained in it. Furthermore, this solid-state was processed like the above and the powder-like high density porous body was obtained. This is a high density porous body concerning a sample 4. In addition, the H₂ O/Si ratio in the raw material in a sample 4 was 2.

[0078] And bulk density and specific surface area were measured by the same approach as the example 1 of an operation gestalt a sample 3 and per four. This result was shown in Table 2. According to this table, as a surfactant, when DTA and OTA were used, the high density porous body which was excellent like the example 1 of an operation gestalt was able to be obtained.

[0079]

[Table 2]
(表 2)

試料No.	界面活性剤	嵩密度 (g/cc)	比表面積 (m ² /g)
3	D T A	0.66	712
4	O T A	0.65	650

DTA… デシルトリメチルアンモニウムブロマイド
OTA… オクチルトリメチルアンモニウムブロマイド

[0080] The example of four examples of an operation gestalt is the adsorption heat pump which used the high density porous body concerning this invention as an adsorbent, as shown in drawing 6. In addition, although this example is a direct-vent-system adsorption pump, the high density porous body of this invention can be used as an adsorbent also in release type adsorption heat pump.

[0081] Next, the direct-vent-system adsorption heat pump 2 of this example is explained. The above-mentioned adsorption heat pump 2 consists of piping 25, 27, and 28 and the bulb 26 which connect mutually an adsorber 21, an evaporator 22, a condenser 23, and these, as shown in drawing 6. And the adsorbate circulates through between these.

[0082] By switching the above-mentioned piping, the above-mentioned adsorbate faces to an adsorber 21 through the adsorption (Ads.) piping 28 in the state of a steam from an evaporator 22. Then, the above-mentioned adsorbate passes along the desorption (Des.) piping 25 from the above-mentioned adsorber 21, and circulates to a condenser 23. Furthermore, the above-mentioned adsorbate is again returned to an evaporator 22 via piping 27 from the above-mentioned condenser 23 after that. In addition, the piping 210,220,230 for heat exchange is formed in the interior of the above-mentioned adsorber 21, an evaporator 22, and a condenser 23.

[0083] And the temperature of an adsorbent is made to go up and down according to the low temperature of temperature Ta and Treg (Ta<Treg), and two hot heat sources. This repeats the cycle through which it circulates from adsorption to desorption. In addition, cold energy (Tcold) can obtain warm temperature (Th) by swerving, swerving and taking out a heat of adsorption [in / for endoergic / in an evaporator 22 / an adsorber 21].

[0084] The adsorbent which consists of a high density porous body concerning this invention is installed in the interior of the above-mentioned adsorber 21 in the above-mentioned adsorption heat pump. Inside the above-mentioned adsorber 21, in order to make easy heat exchange between the above-mentioned adsorbent and a heat carrier, it arranges so that many metal fins may lap. The above-mentioned adsorbent can be made granular and the clearance between the above-mentioned metal fin and a metal fin can be filled up with it. Moreover, a coat can also be carried out to the front face of the above-mentioned metal fin.

[0085] In addition, when carrying out the coat of the above-mentioned adsorbent to especially the above-mentioned metal fin, the coat of the adsorbent may be carried out to it to the metal fin simple substance before attachment by the adsorber 21, respectively. Moreover, after assembling an adsorber 21, the coat of the above-mentioned adsorbent can also be carried out to the metal fin of the interior.

[0086] Since the high density porous body concerning this invention is used as an adsorbent according to this example, the effectiveness that high refrigerating capacity is discovered by use of a little adsorbent can be acquired.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The explanatory view of the high density porous body concerning (a) this invention in the example 1 of an operation gestalt, the explanatory view of the meso porous body of (b) former.

[Drawing 2] The diagram showing the nitrogen adsorption isotherm in the example 1 of an operation gestalt.

[Drawing 3] The diagram showing the pore distribution curve in the example 1 of an operation gestalt.

[Drawing 4] The diagram showing the steam adsorption isotherm in the example 1 of an operation gestalt.

[Drawing 5] The diagram showing the powder X diffraction pattern in the example 1 of an operation gestalt.

[Drawing 6] The explanatory view showing the structure of the adsorption heat pump in the example 4 of an operation gestalt.

[Description of Notations]

1 ... a high density porous body,

[Translation done.]

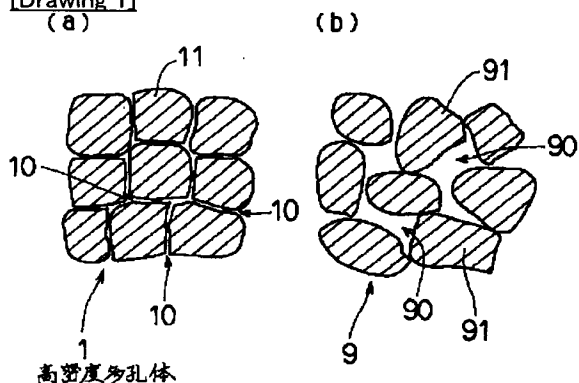
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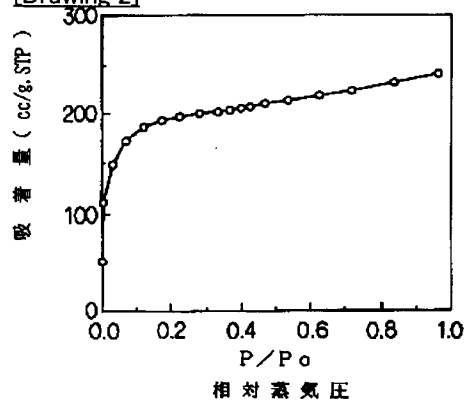
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DRAWINGS

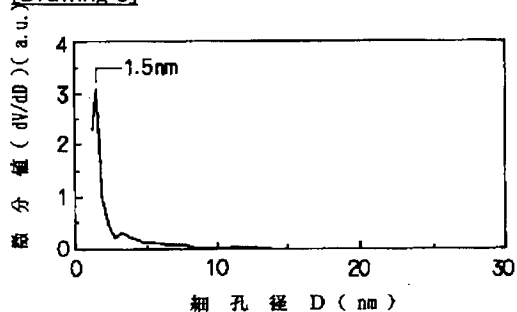
[Drawing 1]



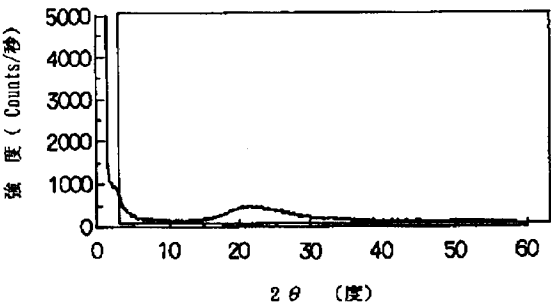
[Drawing 2]



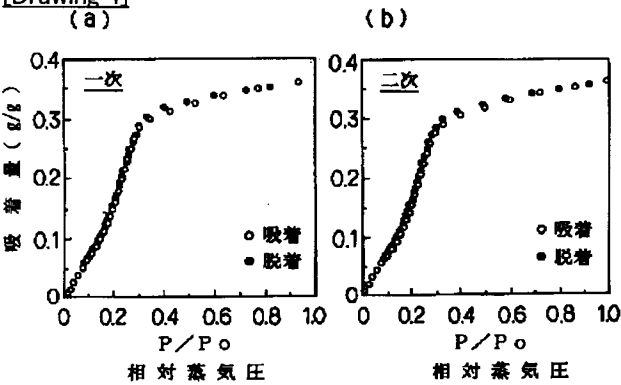
[Drawing 3]



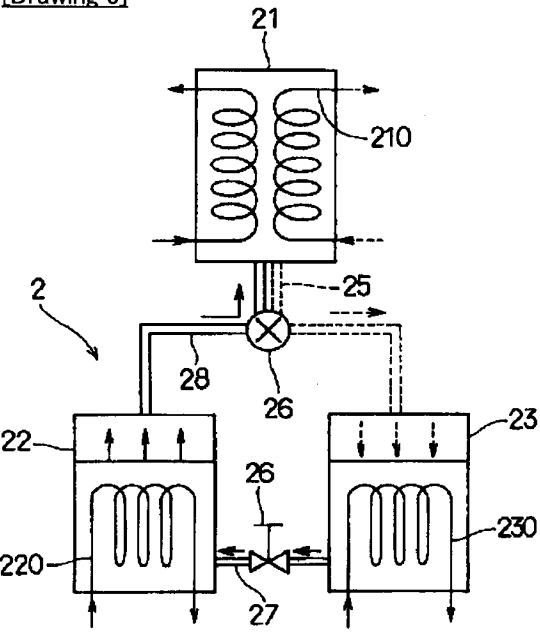
[Drawing 5]



[Drawing 4]
(a)



[Drawing 6]



[Translation done.]

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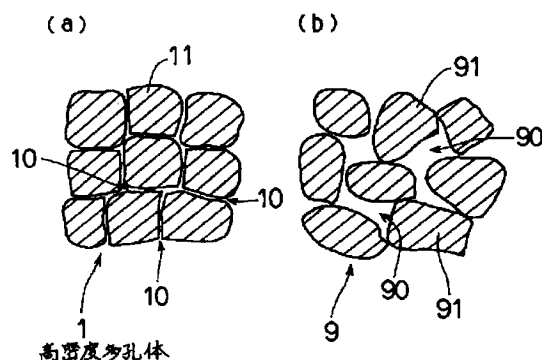
最終頁に続く

(54) 【発明の名称】 高密度多孔体及びその製造方法

(57) 【要約】

【課題】 嵩密度が高く、均一な細孔径を有し、吸着剤または触媒等として使用する際に、その特性を充分発現することができる、高密度多孔体及びその製造方法を提供すること。

【解決手段】 細孔径分布曲線における最大のピークを示す細孔径が1～10nmの範囲内にあり、かつ上記細孔径分布曲線における最大のピークを示す細孔径の-40～+40%の細孔径範囲内に、全細孔容積の60%以上が含まれており、更に、嵩密度が0.5g/cc以上である。原料であるアルコキシラン、水及び界面活性剤を混合、反応させ、シリカ/界面活性剤複合体を形成し、次いで、上記シリカ/界面活性剤複合体から界面活性剤を除去することにより高密度多孔体1を製造するが、上記原料中のH₂O/Siモル比が10以下である。



【特許請求の範囲】

【請求項1】 細孔径分布曲線における最大のピークを示す細孔径が1～10nmの範囲内にあり、かつ上記細孔径分布曲線における最大のピークを示す細孔径の-40～+40%の細孔径範囲内に、全細孔容積の60%以上が含まれており、更に、嵩密度が0.5g/cc以上であることを特徴とする高密度多孔体。

【請求項2】 細孔径分布曲線における最大のピークを示す細孔径が1～10nmの範囲内にあり、かつ水蒸気吸着等温線において、相対蒸気圧が0.2変化したときの吸着量変化が0.1g/cc以上の部分を有することを特徴とする高密度多孔体。

【請求項3】 細孔径分布曲線における最大のピークを示す細孔径が1～10nmの範囲内にあり、かつ粉末X線回折パターンにおいて、1nm以上の範囲内のd値に相当する回折角度に1本以上のピークを持つことを特徴とする高密度多孔体。

【請求項4】 請求項1～3のいずれか一項において、上記高密度多孔体は、全体の80wt%以上が珪素及び酸素よりなることを特徴とする高密度多孔体。

【請求項5】 原料であるアルコキシシラン、水及び界面活性剤を混合、反応させ、シリカ/界面活性剤複合体を形成し、次いで、上記シリカ/界面活性剤複合体から界面活性剤を除去することにより高密度多孔体を製造する方法において、上記原料中のH₂O/Siモル比が10以下であることを特徴とする高密度多孔体の製造方法。

【請求項6】 請求項5において、上記アルコキシシランは、テトラメトキシシランであることを特徴とする高密度多孔体の製造方法。

【請求項7】 請求項5又は6において、上記界面活性剤は、長鎖アルキル基及び親水基を有する化合物であることを特徴とする高密度多孔体の製造方法。

【請求項8】 請求項7において、上記界面活性剤は、アルキルトリメチルアンモニウムであることを特徴とする高密度多孔体の製造方法。

【発明の詳細な説明】

【0001】

【技術分野】 本発明は、溶剤やガソリン等の回収、吸着ヒートポンプ、温度調節、水処理及び脱臭等に用いることができる吸着剤や、排気ガスの浄化、有機合成、石油の改質及びクラッキング等に用いることができる触媒等として使用可能な、高密度多孔体及びその製造方法に関する。

【0002】

【従来技術】 多孔体の中で、特に細孔径（本明細書において、細孔の直径を意味する。）が1～10nmの範囲内にあり、かつ上記細孔径が特に狭い範囲に分布している多孔体をメソ多孔体と称する。上記メソ多孔体の製造方法としては、例えば、層状シリケートに界面活性剤を作

用させて製造する方法がある（特開平4-238810号、特開平6-24867号）。また、シリカ及びSiアルコキシドを界面活性剤と反応させて製造する方法もある（特開平5-503499号）。

【0003】

【解決しようとする課題】 しかしながら、従来の製造方法では、高密度の小さいメソ多孔体しか製造することができなかった。そのため、これらのメソ多孔体を吸着剤または触媒等として用いる場合、吸着剤または触媒等を保持するための充填容器等に比較的少量のメソ多孔体しか充填することができなかった。この場合には、上記メソ多孔体の性能を充分発現させることができなかった。

【0004】 また、上記メソ多孔体の性能を充分発現させるため、該メソ多孔体を充填する充填容器等を大きくすることも考えられる。しかし、充填容器等が大きくなることで、該充填容器等を収納する装置（例えば、吸着ヒートポンプ）が大型化してしまうという問題が生じていた。

【0005】 本発明は、かかる問題点に鑑み、嵩密度が高く、均一な細孔径を有し、吸着剤または触媒等として使用する際に、その特性を充分発現することができる高密度多孔体及びその製造方法を提供しようとするものである。

【0006】

【課題の解決手段】 請求項1の発明は、細孔径分布曲線における最大のピークを示す細孔径が1～10nmの範囲内にあり、かつ上記細孔径分布曲線における最大のピークを示す細孔径の-40～+40%の細孔径範囲内に、全細孔容積の60%以上が含まれており、更に、嵩密度が0.5g/cc以上であることを特徴とする高密度多孔体にある。

【0007】 本発明の作用につき、以下に説明する。本発明の高密度多孔体は、後述する細孔径分布曲線において、上述の特徴を有する。また、その嵩密度が特定の範囲内にある。このような条件を満たす高密度多孔体は、後述の図1（a）に示すごとく、細孔を多量に有するサブミクロンオーダーの一次粒子が集合することにより構成され、該一次粒子同士の間の隙間は大変小さいか、または殆ど存在しない。

【0008】 一方、前述した従来の嵩密度が低いメソ多孔体は、図1（b）に示すごとく、上記と同様のサブミクロンオーダーの一次粒子同士の間に大きな隙間を持った構造を有している。上記メソ多孔体特有の吸着特性または触媒特性等は、主に一次粒子内部の細孔により発現される。本発明の高密度多孔体は、吸着特性または触媒特性等の発現とは関係のない一次粒子同士の間の隙間が大変小さいか、または殆ど存在しない構造を有している。このため、本発明の高密度多孔体においては、吸着特性または触媒特性等を損ねることなく、嵩密度の高い構造を実現することができる。

【0009】以上のように、本発明によれば、高密度が高く、均一な細孔径を有し、吸着剤または触媒等として使用する際に、その特性を充分発現することができる高密度多孔体を得ることができる。

【0010】また、上記に関して、更に詳細に説明する。まず、メソ多孔体における水蒸気の吸着等温線において、相対蒸気圧 (P/P_0) が0.1~0.81で、水蒸気の吸着/脱離が急激に発生することが一般に知ら

$$\ln(P/P_0) = (2VL\gamma \cos \Theta) / (rRT) \dots (1)$$

なお、上記VLは、吸着質が液体状である場合のモル体積、 γ は吸着質が液体状である場合の表面張力、 Θ は接触角、Rは気体定数、Tは絶対温度である。

【0012】ここに吸着質が水蒸気である場合には、 $V_L = 18.05 \cdot 10^{-6} \text{ m}^3 / \text{mol}$ 、 $\gamma = 72.59 \cdot 10^{-3} \text{ N/m}$ 、 $R = 8.3143 \text{ J/deg} \cdot \text{mol}$ 、 $\Theta = 0$ という数値を(1)式に代入することができる。この結果、上記(1)式は、次の(2)式となる $\ln(P/P_0) = -1.058/r \dots (2)$

なお、rの単位はnmである。

【0013】上記(2)式より、細孔径分布において、より細孔径が狭い範囲に分布している場合には、水蒸気の吸着/脱着がより狭いP/P₀の範囲で発生することが分かる。つまり、吸着等温線における、吸着が立ち上がる場所のP/P₀と、吸着が飽和に達した場所のP/P₀の差が小さい。

【0014】本発明の高密度多孔体においては、その細孔径が1~10nmの範囲内にある。そして、上記(2)式より、細孔径が1~10nmの範囲にある場合、吸着等温線における水蒸気の吸着/脱離を起こすP/P₀の範囲は0.12~0.81となる事が分かる。この範囲は、上述したごとく、水蒸気の吸着/脱離が急激に生じる範囲である。これにより、本発明の高密度多孔体(P/P₀が0.12~0.81の範囲において)は、吸着ヒートポンプ、温度調節器等における吸着剤として最適な、小さなP/P₀の変化で大きく吸着量が増加するという特性を有することが分かる。

【0015】なお、上記細孔径分布曲線につき以下に説明する。上記細孔径分布曲線とは、メソ多孔体の細孔径容積(V)を細孔径(D)で微分した値(dV/dD)を細孔径(D)に対しプロットした曲線を示している(図3参照)。上記細孔径分布曲線は、例えば、以下に示す気体吸着法により作成することができる。なお、上記気体吸着法において最もよく用いられる気体は窒素である。

【0016】まず、対象となるメソ多孔体に、液体窒素温度(-196℃)で窒素ガスを導入し、その吸着量を定容量法または重量法において求める。その後、導入する窒素ガスの圧力を徐々に増加させ、各平衡圧に対する窒素ガスの吸着量をプロットすることにより吸着等温線を作成する。この吸着等温線から、例えばCranston-Inclay法、Pollimore-Heal

れている。そして、ある特定のメソ多孔体の吸着等温線が上記条件を満たすか否かは、ケルビン式における細孔径と相対蒸気圧との関係から導くことができる。

【0011】ここにケルビン式とは、メソ多孔体の細孔径(r)と、吸着質が毛管凝縮を起こす相対蒸気圧(P/P₀)との関係を示す式であり、以下の(1)式により示すことができる。

法の計算法を用いて、上記細孔径分布曲線を導くことができる。

【0017】次に、上記請求項1における、『上記細孔径分布曲線における最大のピークを示す直径の+40%の直径範囲には全細孔径容積の60%以上が含まれている』という表現は、以下の状態を表現している。例えば、上述した細孔径分布曲線における最大のピークが2.7nmとなるメソ多孔体αを仮定する。このメソ多孔体αにおいて、細孔径が1.62(=2.7×0.6)~3.78(=2.7×1.4)nmの範囲にある細孔径の容積を総計した細孔径容積Vを求める。一方、上記メソ多孔体αにおいて、全細孔径容積の総計V_{all}を求める。

【0018】そして、V/V_{all}の値が、仮に0.6(60%)以上である場合には、上記メソ多孔体αが本発明にかかる高密度多孔体のひとつであるといえる。または、上記メソ多孔体αの細孔径分布曲線において、細孔径が1.62~3.78nmとなる範囲の積分値が、細孔径分布曲線の全積分面積の60%以上である場合にも、上記メソ多孔体αは本発明にかかる高密度多孔体であるといえる。

【0019】このような条件を満たす本発明の高密度多孔体は、細孔径が狭い範囲に分布しているため、小さなP/P₀の変化に対し、吸着量が大きく変化するという効果を得ることができる。なお、上記細孔径分布曲線における最大のピークを示す直径の+40%の直径範囲に、全細孔径容積の60%未満しか含まれていなかった場合には、P/P₀の変化に対する吸着量変化が小さく、調湿機能や吸着ヒートポンプ特性が十分発現されないおそれがある。

【0020】また、本発明の高密度多孔体の嵩密度は0.5g/cc以上である。このため、上記高密度多孔体を吸着剤または触媒等として使用する際に、充填容器等には、従来と比較して、より多量の高密度多孔体を充填することができる。これにより、より高い吸着特性または触媒特性の発現が可能となる。あるいは、高密度多孔体の充填容器等を小さくすることが可能となり、該充填容器等をセットする装置を小型とすることができる。

【0021】なお、上記嵩密度が0.5g/cc未満である場合には、充填容器等に少量の高密度多孔体しか充填できず、必要な特性が十分に発現されないか、あるい

は、必要な特性を確保するためには、充填容器を大きくする必要があり、装置が大型化して、例えば車載が困難になるおそれがある。

【0022】以上より知られるごとく、本発明の高密度多孔体は、前記のごとき優れた効果を有することが分かる。

【0023】次に、請求項2の発明のように、細孔径分布曲線における最大のピークを示す細孔径が1~10nmの範囲内にあり、かつ水蒸気吸着等温線において、相対蒸気圧が0.2変化したときの吸着量変化が0.1g/cc以上の部分を有することが好ましい。これにより、より少量の多孔体で湿度制御や吸着ヒートポンプ特性が発現されるという効果を得ることができる。なお、上記吸着量変化が、0.1g/cc未満である場合には、多量の多孔体が必要となり、充填容器や装置全体が大型化するという問題を生じるおそれがある。

【0024】なお、上記『相対蒸気圧が0.2変化したときの吸着量変化が0.1g/cc以上の部分を有する』とは、水蒸気吸着等温線において、相対蒸気圧(P/P0)が0.1と0.3の時の吸着量がそれぞれ $V_{0.1} = 0.2 \text{ g/cc}$ 、 $V_{0.3} = 0.5 \text{ g/cc}$ としたとき、相対蒸気圧が0.2変化したときの吸着量変化は $V_{0.3} - V_{0.1} = 0.3 \text{ g/cc}$ となり、「0.1g/cc以上」に該当する、との意味である。相対蒸気圧の変化は0~1のどの範囲においてでも良く、又、吸着量変化が0.1g/cc以上の部分が高密度多孔体の一部だけであっても良い。

【0025】次に、請求項3の発明のように、細孔径分布曲線における最大のピークを示す細孔径が1~10nmの範囲内にあり、かつ粉末X線回折パターンにおいて、1nm以上の範囲内のd値に相当する回折角度に1本以上のピークを持つことが好ましい。これは、1nm以上の周期的な結晶構造が高密度多孔体中に存在することを示しており、細孔径が1~10nmの範囲内にあり、かつ細孔径が均一な分布であることを示す。これにより、例えば水蒸気等が狭いP/P0の範囲内で吸・脱着を起こす、という吸着ヒートポンプや調湿剤としての優れた特性を持つことが分かる。

【0026】次に、請求項4の発明のように、上記高密度多孔体は、全体の80wt%以上が珪素及び酸素よりなることが好ましい。これにより、吸着分子(例えば水分子)と多孔体表面との結合は比較的弱いものとなり、吸着した分子が比較的脱離し易く、可逆的に吸・脱着を繰り返すことができる。なお、珪素及び酸素の含有率が80wt%未満である場合には、珪素と酸素とは異なる元素が混合されることにより、表面に固体酸性等が発現され、吸着分子が容易に脱離しないおそれがある。

【0027】次に、請求項5の発明は、原料であるアルコキシシラン、水及び界面活性剤を混合、反応させ、シリカ/界面活性剤複合体を形成し、次いで、上記シリカ

/界面活性剤複合体から界面活性剤を除去することにより高密度多孔体を製造する方法において、上記原料中の $\text{H}_2\text{O}/\text{Si}$ モル比が10以下であることを特徴とする高密度多孔体の製造方法にある。

【0028】上記『原料中の $\text{H}_2\text{O}/\text{Si}$ モル比』とは、上記原料の混合において、添加した H_2O の総量に対する他の原料に含有されるSiの総量の比を示している。上記『 $\text{H}_2\text{O}/\text{Si}$ モル比』が10以下であることにより、製造した多孔体の密度を高めることができる。なお、上記『 $\text{H}_2\text{O}/\text{Si}$ モル比』が10より大きい場合には、例えば、アルコキシシランが加水分解・縮合して生成するシリカの微粒子同士の隙間が大きくなり、結果として、生成したシリカの密度が低下するおそれがある。よって、高密度多孔体を得ることができなくなるおそれがある。

【0029】また、上記『 $\text{H}_2\text{O}/\text{Si}$ モル比』の下限は1以上であることが好ましい。上記値が1未満である場合には、アルコキシシランの加水分解が起らず、結果としてシリカが得られないおそれがある。よって、高密度多孔体を得ることができなくなるおそれがある。

【0030】次に、上記原料の混合方法としては、特に限定しないが、最初にアルコキシシランに水を添加し、室温で10分~3時間攪拌した後に、界面活性剤を添加することが好ましい。また、上記水は、上記アルコキシシランが含有する珪素1モルに対し、0.5~10モル添加することが好ましい。この混合方法により、アルコキシシランが直鎖状のアルコキシシラン重合物を経て、ゆっくり縮合することにより、ち密なシリカの組織が形成され、密度が高まるという効果を得ることができる。

【0031】上記水の添加量が0.5モル未満である場合には、アルコキシシランの加水分解が不十分となり、強固な高密度多孔体の骨格が形成されない、あるいは多孔体の密度が低下するおそれがある。一方、10モルよりも多く添加した場合には、アルコキシシランの加水分解及び縮合が急速に行われ、シリカ組織が粗となり高密度多孔体の密度が低下するおそれがある。

【0032】また、上記攪拌時間が10分未満である場合には、高密度多孔体の密度が低下するおそれがある。一方、3時間を越えた場合には、均一な細孔が形成されないおそれがある。

【0033】更に、上記混合の際には、pH調整剤として少量の酸を添加することが好ましい。これにより、各成分が溶解しやすくなり、均一な溶液が調製しやすくなる。そして、上記混合の際のpHは1~4の範囲に調整されることが好ましい。上記pHが1未満である場合には、加水分解及び縮合が急速に進行し、均一な細孔の形成が妨げられるおそれがある。あるいは、生成した多孔体の密度が低下するおそれがある。一方、上記pHが4より大きい場合には、各成分の溶解が不十分であり、必要な加水分解が行われないおそれがある。また、上記酸

としては、希塩酸（例えば2規定）を用いることができるが、硫酸等の他の酸でもよい。

【0034】また、上記界面活性剤は粉末のまま添加してもよいが、少量の水に溶解させて添加してもよい。そして、上記界面活性剤の添加量は、全原料中に含有されるSi1モルに対して、1～10モルとなるように添加することが好ましい。上記界面活性剤の添加量が10モルより多い場合には、上記シリカ／界面活性剤複合体の形成に寄与しない余剰の界面活性剤が、上記シリカ／界面活性剤複合体に混在し、高密度多孔体の密度が低下するあるいは製造コストが高くなるおそれがある。

【0035】一方、上記添加量が1モル未満である場合には、上記シリカ／界面活性剤複合体の形成に寄与しない余剰のシリカが、上記シリカ／界面活性剤複合体に混在し、均一な細孔が形成されている部分の比率が低下し、必要な機能が充分発現されないおそれがある。更に、上記シリカがシリカ／界面活性剤の表面に厚い層を形成して付着し、これにより得られた高密度多孔体の細孔容積が減少するおそれもある。

【0036】次いで、上記シリカ／界面活性剤複合体から界面活性剤を除去し、高密度多孔体となす方法につき説明する。即ち、上記シリカ／界面活性剤複合体は原料を混合した溶液において生成されるが、まずはこの溶液中よりシリカ／界面活性剤複合体を分離する。その後、得られた単独のシリカ／界面活性剤複合体より界面活性剤を除去し、高密度多孔体となす。これらの工程につき、以下に説明する。

【0037】まず、シリカ／界面活性剤を含有した溶液は、そのまま放置すると次第に溶液全体が均一な状態を保ったまま固化する。従って、上記溶液を、密閉容器中、あるいは開放容器中において放置することにより、上記溶液は塊状となる。これにより得られた塊を乾燥した後、粉砕する。更にその後、ふるいにかけて、粉砕物の粒径を揃える。これにより、所望の粒径を有する粉末状のシリカ／界面活性剤複合体を得ることができる。

【0038】また、上記溶液をアルミニウム等よりなる基板の上にコートし、放置する。これにより、上記溶液は基板の上で固化し、膜状のシリカ／界面活性剤複合体を得ることができる。なお、上記基板に溶液をコートする方法としては、スピンコート法、キャスト法、ディップコート法等が挙げることができる。

【0039】次に、上記粉末状あるいは膜状のシリカ／界面活性剤複合体より界面活性剤を除去し、高密度多孔体となす。この除去方法としては、例えば、焼成による方法と、溶剤を使用する方法とが挙げられる。まず、焼成による除去方法を示す。上記シリカ／界面活性剤複合体を、400℃～1000℃の範囲で、好ましくは500℃～700℃の範囲で加熱する。上記加熱時間は30分以上とすれば、実用上において差し支えない程度に界面活性剤を除去することができる。しかし、上記シリ

カ／界面活性剤複合体より、上記界面活性剤を完全に除去するためには、1時間以上加熱することが好ましい。

【0040】また、上記加熱温度が400℃未満である場合には、温度が低すぎるため、界面活性剤を十分に燃焼除去することができないおそれがある。また、上記加熱温度が1000℃を越えた場合には、温度が高すぎるために、細孔構造が崩壊するおそれがある。なお、上記加熱に当たっての雰囲気は空気を流通させればよい。しかし、多量の燃焼ガスが発生するため、加熱の初期は、窒素ガス等の不活性ガスを流通させることがより好ましい。

【0041】次に、溶剤を使用する除去方法を示す。まず、界面活性剤に対する溶解度の大きい溶媒に少量の陽イオン成分を添加した溶剤を作成する。上記溶剤に、上記シリカ／界面活性剤複合体を分散させ、攪拌する。これにより、上記シリカ／界面活性剤複合体より、界面活性剤が溶剤中に溶解し、分離する。その後、上記溶剤より固形分を回収する。上記固形分が求める高密度多孔体である。

【0042】上記溶媒としては、例えば、エタノール、メタノール等のアルコール、またアセトン等を使用することができる。また、上記陽イオン成分を溶媒に添加するためには、該溶媒に以下の物質を添加することが好ましい。上記物質としては、塩酸、酢酸、塩化ナトリウム、塩化カリウム等を使用することができる。これにより、一層効率よく上記界面活性剤を上記シリカ／界面活性剤複合体より分離することができる。

【0043】そして、上記陽イオンの添加濃度は、上記溶媒に対して、0.1～10モル／リットルとすることが好ましい。上記添加濃度が0.1モル／リットル未満である場合には、界面活性剤の分離が不十分であり、高密度多孔体に界面活性剤が残存するおそれがある。一方、上記添加濃度が10モル／リットルより大きい場合には、それ以上添加する効果がなく、コスト高となるおそれがある。また、高密度多孔体のシリカ骨格が崩壊するおそれがある。

【0044】次に、上記溶媒に対するシリカ／界面活性剤複合体の分散量は、溶剤100ccに対し、0.5～50gであることが好ましい。0.5g未満である場合には、シリカ／界面活性剤複合体の処理効率が悪く、溶剤のコストや製造コストがかかるおそれがある。一方、50gより多い場合には、界面活性剤の分離が不十分であり、高密度多孔体中に界面活性剤が残存するおそれがある。

【0045】また、上記溶剤にシリカ／界面活性剤複合体を分散させた後の攪拌は、25～100℃の温度範囲において行うことが好ましい。これにより、界面活性剤の分離のため処理時間が短縮することができる。上記温度が25℃未満である場合には、処理時間の短縮が期待されないおそれがある。一方、100℃を越えた場合に

は、加熱するためのエネルギーコストがかかる、あるいは溶剤の揮発によるロスが多くなるおそれがある。

【0046】なお、上記高密度多孔体は、粉末とし、その粒径ごとくふるい分け、また使用目的に応じた形状に成形することができる。そして、これらのふるい分け、成形の工程は、上記界面活性剤を除去する工程の前に行うことができる。この場合には、成形時の細孔の崩壊を妨げる、あるいは成形強度が向上するという効果を得ることができる。また、最終的に要求される形状に上記シリカ／界面活性剤を成形した後に、界面活性剤の除去を行い、高密度多孔体とすることもできる。この場合には、成形時の細孔の崩壊を防止することができる。また、成形強度を高めることができる。

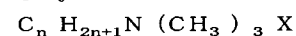
【0047】次に、上記原料におけるアルコキシシランとしては、テトラメトキシシラン、テトラエトキシシラン、テトラプロポキシシランあるいはメチルトリメトキシシラン等のアルキルアルコキシシラン等を用いることができる。これらの1種類あるいは2種類以上の組み合わせでもよい。

【0048】そして、請求項6の発明によれば、上記アルコキシシランは、特にテトラメトキシシランであることが好ましい。これにより、比較的容易に高密度多孔体を製造することができる。

【0049】また、請求項7の発明のように、上記界面活性剤は、長鎖アルキル基及び親水基を有する化合物であることが好ましい。この化合物を使用することにより、反応溶液中で界面活性剤の分子集合体を形成され、その分子集合体の大きさに対応した1～10nmの均一な細孔が高密度多孔体に形成されるという効果を得ることができる。

【0050】また、上記アルキル基としては、炭素原子数が2～18のものが好ましい。これらのアルキル基よりなる界面活性剤を使用することにより、上記の分子集合体が効率的に形成されるという効果を得ることができる。なお、上記炭素原子数が18よりも多い場合には、その様な界面活性剤は市販されておらず、コストがかかるおそれがある。また、炭素原子数が1である場合、つまり上記アルキル基がメチル基である場合には、上記の分子集合体が形成され難く、1～10nmの均一な細孔が形成されないおそれがある。また、上記親水基としては、例えば、 $-N^+(CH_3)_3$ 、 $=N^+(CH_3)_2$ 、 $\equiv N^+(CH_3)$ 、 $\equiv N^+$ 、 $-NH_2$ 、 $-NO$ 、 $-OH$ 、 $-COOH$ 等が挙げられる。

【0051】次に、上記界面活性剤としては、以下の化学式に示される化合物を使用することができる。また、このような化合物としては、請求項8の発明のように、アルキルトリメチルアンモニウムを使用することが好ましい。



ここに、nは2～18の整数、Xは、例えば、塩化物イ

オン、臭化物イオン等のハロゲン化物イオンである。

【0052】このような界面活性剤を使用することにより、反応溶液中で界面活性剤の分子集合体が効率的に形成され、その分子集合体に対応した1～10nmの均一な細孔が形成され易いという効果を得ることができる。なお、上記化学式による界面活性剤の具体例としては、ヘキサデシルトリメチルアンモニウムクロライド、テトラデシルトリメチルアンモニウムクロライド、デシルトリメチルアンモニウムブロマイド、デシルトリメチルアンモニウムブロマイド、オクチルトリメチルアンモニウムブロマイド等を挙げるることができる。

【0053】

【発明の実施の形態】

実施形態例1

本発明の実施形態例にかかる高密度多孔体及びその製造方法、またその性能につき、図1～図5、表1を用いて説明する。本例の高密度多孔体は、細孔径分布曲線における最大のピークを示す細孔径が1～10nmの範囲内にあり、かつ上記細孔径分布曲線における最大のピークを示す細孔径の-40～+40%の細孔径範囲内に、全細孔容積の60%以上が含まれており、更に、嵩密度が0.5g/cc以上である。

【0054】そして、図1(a)に示すごとく、このような条件を満たす高密度多孔体1は、細孔を多量に有するサブミクロンオーダーの一次粒子11が集合することにより構成され、該一次粒子同士11の間の隙間10は大変小さいか、または殆ど存在しない。

【0055】また、本例にかかる上記高密度多孔体1を製造するに当たっては、原料であるアルコキシシラン、水及び界面活性剤を混合、反応させ、シリカ／界面活性剤複合体を形成し、次いで、上記シリカ／界面活性剤複合体から界面活性剤を除去する。そして、上記原料中の H_2O/Si モル比は10以下の範囲内にある。

【0056】次に、本発明にかかる高密度多孔体1である試料1、2と、従来のメソ多孔体である比較試料C1、C2とを性能比較する方法等につき説明する。まず本発明にかかる高密度多孔体1である試料1、2の製造方法につき具体的に説明する。

【0057】アルコキシシランであるテトラメトキシシラン(TMOS)15.2gに水3.6g及び2Nの塩酸約0.1gを添加し、室温で1時間攪拌した。この添加と攪拌とにより得られた溶液に、界面活性剤であるドデシルトリメチルアンモニウムブロマイド(DDTA)7.71gを更に添加し、数分間激しく攪拌し、溶液に粘性を生じせしめた。更に得られた溶液を密閉容器中において、2～3日放置した。以上により、透明で均一な固体を得た。この固体が、シリカ／界面活性剤複合体である。

【0058】上記シリカ／界面活性剤複合体を乾燥し、その後550℃、6時間、空気中において、焼成し、該

シリカ／界面活性剤複合体より、界面活性剤を除去した。上記焼成により得られた固体を粉碎し、ふるいを使用して、粒径 $100\sim150\mu\text{m}$ に揃えた。以上により、粒径 $100\sim150\mu\text{m}$ の粉末状の高密度多孔体を得た。これが試料1にかかる高密度多孔体である。なお、試料1における原料中の $\text{H}_2\text{O}/\text{Si}$ 比は2であった。

【0059】また、上記製造方法において、TMOS 15.2gに水3.6g及び2Nの塩酸約0.1gを添加し、室温で1時間攪拌することにより得られた溶液に、DDTA 7.71g及び H_2O 3.6gの混合物を添加した。その他のプロセスは、上記試料1と同様である。この製造方法により得られた高密度多孔体が試料2である。そして、試料2における原料中の $\text{H}_2\text{O}/\text{Si}$ 比は4であった。

【0060】また、上記製造方法において、TMOS 15.2gに水3.6g及び2Nの塩酸約0.1gを添加し、室温で1時間攪拌することにより得られた溶液に、DDTA 7.71g及び H_2O 1.8gの混合物を添加した。その他のプロセスは上記試料1と同様である。この製造方法により得られたメソ多孔体が比較試料C1である。そして、比較試料1における原料中の $\text{H}_2\text{O}/\text{Si}$ 比は1.2であった。

【0061】また、上記製造方法において、TMOS 15.2gに水3.6g及び2Nの塩酸約0.1gを添加し、室温で1時間攪拌することにより得られた溶液に、DDTA 7.71g及び H_2O 3.6gの混合物を添加した。その他のプロセスは試料1と同様である。この製造方法により得られたメソ多孔体が比較試料C2である。そして、比較試料2における原料中の $\text{H}_2\text{O}/\text{Si}$ 比は2.2であった。

【0062】以上により得られた試料1、2及び比較試料C1、C2の嵩密度及び比表面積を測定した。上記嵩密度は、各試料1、2及び比較試料C1、C2の重量と体積を、重量計及びメスシリンダーにより秤することにより求めた。上記比表面積は、大倉理研の自動比表面積測定装置により、BET一点法により求めた。上記測定結果を表1に示す。

【0063】同表によれば、試料1、2は、比較試料C1、C2よりも高い嵩密度を有することが分かった。また、試料1、2は、比較試料C1、C2よりも高い比表面積を有することが分かった。従って、試料1、2は比較試料C1、C2と比較して、吸着特性または触媒特性等において優れていることが分かった。また、試料1、2は、より高い嵩密度を有しているため、同体積の充填容器に充填する場合においても、比較試料C1、C2に比べて、より多くの量を充填することができ、吸着特性または触媒特性等の性能を充分発現させることができることが分かった。

【0064】次に、試料1の、窒素吸着等温線、細孔径

分布曲線、水蒸気吸着等温線及び粉末X線回折を測定あるいは計算し、図2～図5に示した。まず、図2は窒素吸着等温線である。これは液体窒素温度において、定容量法により測定した。また、図3は細孔分布曲線である。これは図2に示した窒素吸着等温線から、Cranston-Incaly法を用い、計算した。

【0065】また、図4は水蒸気等温線である。これは日本ベル製のBELSORP18を使用し、 25°C において定容量法により測定した。また、図5は粉末X線回折パターンである。これは理学RAD-B装置を用い、 $\text{CuK}\alpha$ をX線源として、 $2^\circ(2\theta)/\text{分}$ にてスキャンすることにより得られた。なお、スリット幅は $1^\circ-0.3\text{mm}-1^\circ$ であった。

【0066】図2の窒素吸着等温線より、試料1は、低相対蒸気圧(P/P_0)から高い吸着性を示し、 $P/P_0=0.2$ で窒素ガス(STP、標準条件)にして、 200cc/g の吸着量を示した。この値から、試料1にかかる高密度多孔体の細孔容積が 0.31cc/g であることが分かった。次に、図3の細孔径分布曲線から、試料1にかかる高密度多孔体の細孔径が 1.5nm であることが分かった。

【0067】図4の水蒸気吸着等温線では、試料1は、 $P/P_0=0\sim0.3$ の範囲内で大きく吸着量が変化するという特性を示した。 $P/P_0=0.1$ と $P/P_0=0.3$ の時の水蒸気の吸着量は、それぞれ 0.07g/g と 0.28g/g であった。高密度多孔体 0.71g/cc で、嵩あたりの吸着量に変換すると、それぞれ、 0.05g/cc と 0.2g/cc となり、その差は 0.15g/cc となる。即ち、試料1は請求項2の高密度多孔体となる。そして、吸着側と脱着側との等温線はほぼ一致し、ヒステリシスを示さなかった。

【0068】また、同一の試料1を使用して2回目の水蒸気吸着等温線(二次)を測定した。しかし、1回目(一次)の水蒸気吸着等温線とほぼ同形状であったことから、水蒸気の吸着により、試料1の構造が変化しないことが分かった。

【0069】図5の粉末X線回折パターンでは、回折角が $1^\circ\sim60^\circ$ の範囲において、明確なピークが観察されなかった。よって、試料1は、規則的な結晶構造は有していないことが分かった。

【0070】以上より、試料1は規則的な結晶構造は有していないが、 1.5nm を中心とする均一な細孔と高い嵩密度を有していることが分かった。

【0071】

【表1】

(表1)

	試料No.	H ₂ O/Si モル比	嵩密度 (g/cc)	比表面積 (m ² /g)
本 発 明	1	2	0.71	1066
	2	4	0.55	1022
比 較 例	C 1	1 2	0.38	950
	C 2	2 2	0.35	765

【0072】実施形態例2

本例は、実施形態例1とは異なる高密度多孔体の製造方法であって、原料を混合した溶液において生成されたシリカ/界面活性剤複合体を分離するにあたり、基板に溶液をコートする方法を採用した製造方法である。

【0073】TMOS15.2gに水3.6g及び2Nの塩酸約0.1gを添加し、室温で1時間攪拌した。この添加と攪拌とにより得られた溶液に、DDTA7.71gを更に添加し、数分間激しく攪拌し、溶液に粘性を生じせしめた。更に得られた溶液をアルミニウム板の表面にコートして、室温で2～3日放置した。以上により、上記アルミニウム板の表面において、均一な透明膜を得た。この透明膜がシリカ/界面活性剤複合体である。

【0074】その後、上記透明膜であるシリカ/界面活性剤複合体を乾燥し、次いで、550℃、6時間、空気中において焼成した。以上により、本発明にかかる高密度多孔体を得た。なお、本例の製造方法においても、その原料中のH₂O/Si比は2であった。その他は、実施形態例1と同様である。

【0075】実施形態例3

本例は、実施形態例1に示す試料1、2に用いた界面活性剤とは異なる界面活性剤を用いて製造した試料3、4の性能につき説明するものである。試料3、4の製造方法につき、説明する。TMOS15.2gに水3.6g及び2Nの塩酸約0.1gを添加し、室温で1時間攪拌した。この添加と攪拌とにより得られた溶液に、界面活性剤であるデシルトリメチルアンモニウムブロマイド

(DTA)7.01gを更に添加し、数分間激しく攪拌し、溶液に粘性を生じせしめた。更に、得られた溶液を密閉容器中において、2～3日放置した。以上により、透明で均一な固体を得た。この固体がシリカ/界面活性剤複合体である。

【0076】上記シリカ/界面活性剤複合体を乾燥し、その後550℃、6時間、空気中において、焼成し、該シリカ/界面活性剤複合体より、界面活性剤を除去した。上記焼成により得られた固体を粉砕し、ふるいを使用して、粒径100～150μmに揃えた。以上により、粒径100～150μmの粉末状の高密度多孔体を得た。これが試料3にかかる高密度多孔体である。なお、試料3における原料中のH₂O/Si比は2であつ

た。

【0077】また、上記添加と攪拌とにより得られた溶液に、界面活性剤としてオクチルトリメチルアンモニウムブロマイド(OTA)6.31gを添加し、上記と同様に処理して、透明で均一な固体を得た。更に、この固体を、上記と同様に処理して、粉末状の高密度多孔体を得た。これが試料4にかかる高密度多孔体である。なお、試料4における原料中のH₂O/Si比は2であつた。

【0078】そして、試料3、4につき、実施形態例1と同様の方法にて、嵩密度及び比表面積を測定した。この結果を表2に示した。同表によれば、界面活性剤として、DTA、OTAを使用した場合においても、実施形態例1と同様に優れた高密度多孔体を得ることができた。

【0079】

【表2】

(表2)

試料No.	界面活性剤	嵩密度 (g/cc)	比表面積 (m ² /g)
3	D T A	0.66	712
4	O T A	0.65	650

DTA…デシルトリメチルアンモニウムブロマイド
OTA…オクチルトリメチルアンモニウムブロマイド

【0080】実施形態例4

本例は、図6に示すごとく、本発明にかかる高密度多孔体を、吸着剤として使用した吸着ヒートポンプである。なお、本例は密閉式吸着ポンプであるが、本発明の高密度多孔体は、解放式吸着ヒートポンプにおいても、吸着剤として使用することができる。

【0081】次に、本例の密閉式吸着ヒートポンプ2について説明する。上記吸着ヒートポンプ2は、図6に示すごとく、吸着器21、蒸発器22、凝縮器23、そしてこれらを互いに連結する配管25、27、28及びバルブ26よりなる。そして、これらの間を吸着質が循環している。

【0082】上記配管を切り換えることにより、上記吸着質は蒸気の状態では蒸発器22から吸着(Ads.)配管28を通り吸着器21へ向かう。その後、上記吸着質は、上記吸着器21から脱着(Des.)配管25を通り、凝縮器23へと循環する。更に、その後、上記吸着質は、上記凝縮器23より、配管27を経由して再び蒸発器22へと戻される。なお、上記吸着器21、蒸発器22、凝縮器23の内部には、熱交換用配管210、220、230が設けてある。

【0083】そして、温度Ta及びTreg(Ta<Treg)の低温及び高温の二つの熱源により、吸着剤の

温度を上下させる。これにより、吸着から脱着へと循環するサイクルを繰り返す。なお、冷熱 (T cold) は、蒸発器 2 2 における吸熱を、温熱 (T h) は吸着器 2 1 における吸着熱をそれぞれ取出すことにより得ることができる。

【0084】本発明にかかる高密度多孔体よりなる吸着剤は、上記吸着ヒートポンプにおける上記吸着器 2 1 の内部に設置されている。上記吸着器 2 1 の内部には、上記吸着剤と熱媒体との間の熱交換を容易にするため、多数の金属フィンが重なるように配置してある。上記吸着剤は粒状にして、上記金属フィンと金属フィンとの間の隙間に充填することができる。また、上記金属フィンの表面にコートすることもできる。

【0085】なお、特に上記金属フィンに、上記吸着剤をコートする場合には、吸着器 2 1 への組付け前の金属フィン単体に対し、それぞれ吸着剤をコートしてもよい。また、吸着器 2 1 を組み立てた後に、その内部の金属フィンに対し、上記吸着剤をコートすることもできる。

【0086】本例によれば、本発明にかかる高密度多孔体を吸着剤として使用しているため、少量の吸着剤の使用で、高い冷凍能力が発現されるという効果を得ることができる。

【0087】

【発明の効果】上記のごとく、本発明によれば、嵩密度が高く、均一な細孔径を有し、吸着剤または触媒等として使用する際に、その特性を充分発現することができる高密度多孔体及びその製造方法を提供することができる。

【図面の簡単な説明】

【図 1】実施形態例 1 における、(a) 本発明にかかる高密度多孔体の説明図、(b) 従来のメソ多孔体の説明図。

【図 2】実施形態例 1 における、窒素吸着等温線を示す線図。

【図 3】実施形態例 1 における、細孔分布曲線を示す線図。

【図 4】実施形態例 1 における、水蒸気吸着等温線を示す線図。

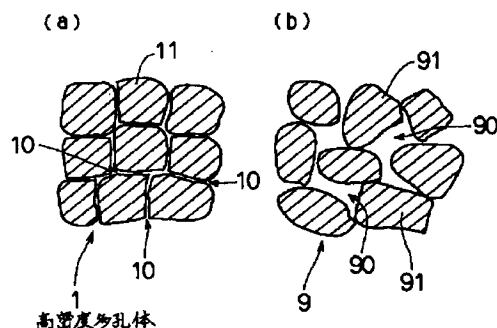
【図 5】実施形態例 1 における、粉末 X 線回折パターンを示す線図。

【図 6】実施形態例 4 における、吸着ヒートポンプの構造を示す説明図。

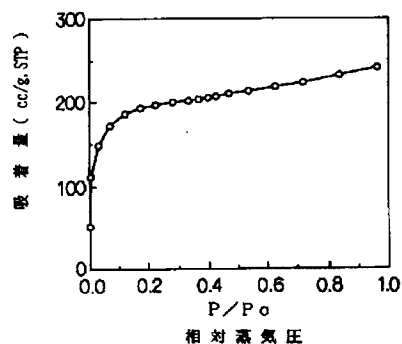
【符号の説明】

1... 高密度多孔体、

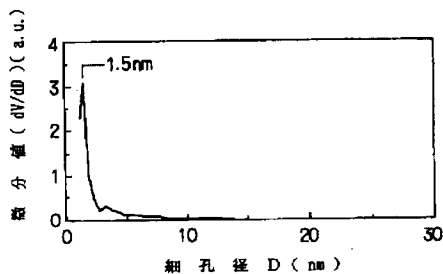
【図 1】



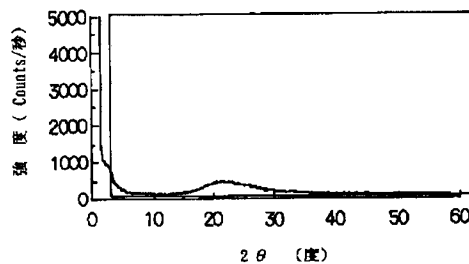
【図 2】



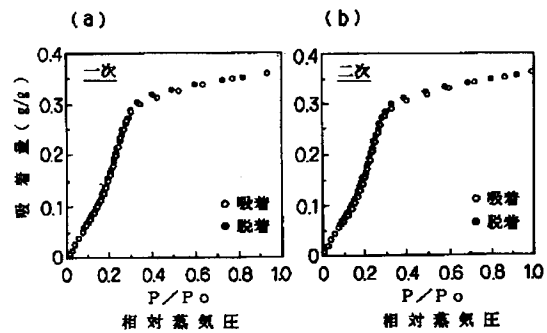
【図 3】



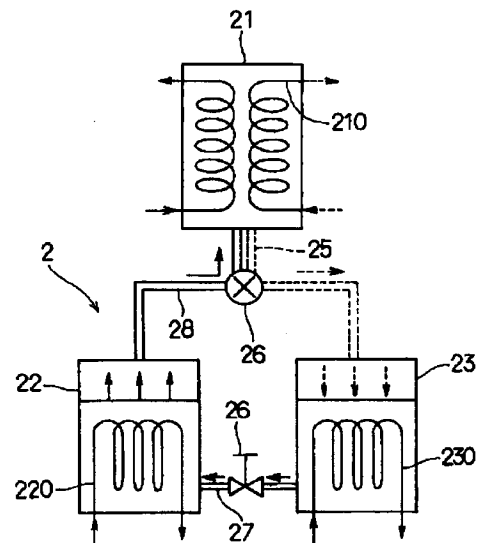
【図 5】



【図4】



【図6】



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